

LIGAND SUBSTITUTION REACTIONS ON Fe(III), Mn(III) AND Pd(II) CENTRES: KINETIC AND MECHANISTIC INVESTIGATIONS

A Thesis Submitted
In Partial fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by

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to the

DEPARTMENT OF CHEMISTRY
**INDIAN INSTITUTE OF TECHNOLOGY
KANPUR, INDIA**

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To
my parents
with regards

STATEMENT

I, hereby, state that the matter contained in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Professor P.C. Nigam.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been given wherever the work described is based on the findings of other investigators.

A handwritten signature in cursive script, appearing to read 'Mishra', is written over a horizontal line.

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CERTIFICATE I

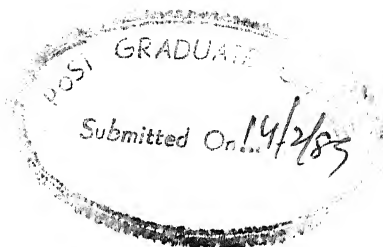
This is to certify that Pratima Kumari Mishra has satisfactorily completed all the courses required for the Ph.D. programme. These courses are listed below:

Chm 505N Principles of Organic Chemistry
Chm 521N Chemical Binding
Chm 524N Modern Methods in Physical Chemistry
Chm 525N Principles of Physical Chemistry
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Chm 542N Advanced Inorganic Chemistry II
Chm 632N Enzyme Reaction Mechanism and
Enzyme Kinetics
Chm 800N General Seminar
Chm 801N Special Seminar
Chm 900N Post Graduate Research

Pratima Kumari Mishra was admitted to the candidacy of the Ph.D. degree on 17th October 1985 after she successfully completed the written and oral qualifying examinations.

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CERTIFICATE II

Certified that the work contained in this thesis titled, 'LIGAND SUBSTITUTION REACTIONS ON Fe(III), Mn(III) AND Pd(II) CENTRES: KINETIC AND MECHANISTIC INVESTIGATIONS' has been carried out by Pratima Kumari Mishra under my supervision and the same has not been submitted elsewhere for a degree.

P. C. Nigam

(P.C. Nigam)
Thesis Supervisor

Kanpur

February 1989

ACKNOWLEDGEMENTS

Despite the impossibility of giving credit to everyone who has been of help, I would like to single out certain people who have been especially instrumental, directly or indirectly, in completing this work.

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Finally I express my sincere thanks to the authorities of Indian Institute of Technology, Kanpur and Council of Scientific and Industrial Research, New Delhi, India, for the financial assistance provided to me for carrying out this work.

Pratima Kumari Mishra

PREFACE

Kinetic investigations followed by postulation of reaction mechanisms are of immense value in understanding and systematizing of a wide variety of chemical reactions. The purpose of work embodied in the thesis is to obtain a better understanding of ligand substitution reactions in general and substitution reactions on Fe(III), Mn(III) and Pd(II) metal centres in particular. The ligands chosen for this investigation are the polydentate ligands e.g. polyaminocarboxylates and the displacing species are the monodentate cyanide ions. The presentation is divided in five chapters.

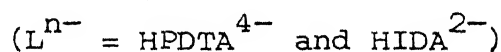
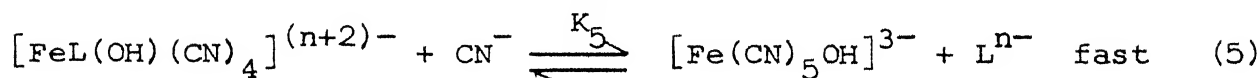
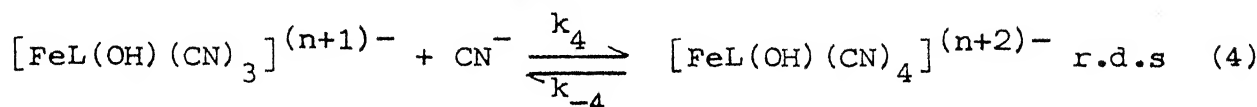
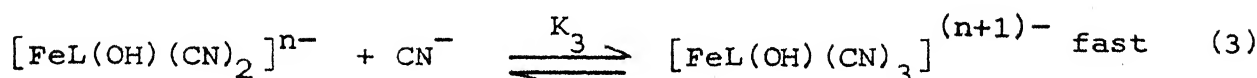
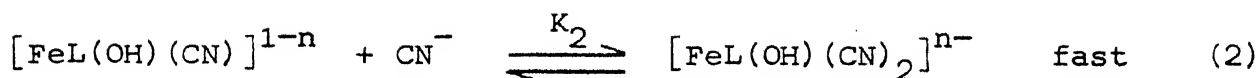
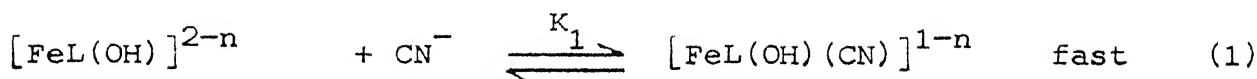
Chapter I is introductory. It comprises of a survey of the general features of ligand substitution reactions with particular emphasis on substitution reactions on Fe(III), Mn(III) and Pd(II) complexes. A brief treatment is also given to the importance and applications of ligand substitution reactions in various branches of chemistry.

The kinetics and mechanism of substitution reactions on the aminopolycarboxylato ferrate(III) complexes by the cyanide ions have been reported in chapter II. The aminocarboxylates chosen are HPDTA⁴⁻ (2-hydroxy 1,3-diaminopropanetetraacetate anion) and HIDA²⁻, (hydroxyethyl)iminodiacetate anion. The reactions

have been followed spectrophotometrically at 395 nm (λ_{max} of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$) in presence of excess cyanide ions at $25 \pm 0.1^\circ\text{C}$, $\text{pH} = 10.5 \pm 0.02$ and $I = 0.25\text{M}$ (NaClO_4) for HPDTA^{4-} , and at $25 \pm 0.1^\circ\text{C}$, $\text{pH} = 9.5 \pm 0.02$ and $I = 0.1\text{M}$ (NaClO_4) for HIDA^{2-} systems. A detailed investigation shows that three reactions are occurring in this reaction system,

- (1) Formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and L^{n-} from $[\text{FeL}(\text{OH})^{2-n}]$
- (2) Conversion of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$
- (3) Reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ by the ligands L^{n-} released in the first stage.

A variable order dependence in cyanide in the forward reaction and an inverse-first-order dependence in cyanide, during the reverse reaction makes it possible to pin point the rate-determining step as the penultimate one in a five step mechanism. Activation parameters (both for forward and reverse reaction), effect of pH and ionic strength on the forward rate constants have been used to support the proposed mechanism given from equation (1-5). In subsequent narration the polydentate ligands will be represented by L^{n-} .



An interesting free energy relationship (equation.6) has been discovered between the stepwise rate constants k'_n ($k'_n = k_4 K_3 K_2 K_1$ (4th order), $k_4 K_3 K_2$ (3rd order), $k_4 K_3$ (2nd order) and k_4 (1st order) and the over all stability constants β_{lmn} of the intermediates viz. $[\text{FeL}(\text{OH})(\text{CN})_x]$ ($x = 0, 1, 2$ and 3 respectively) reacting in the particular steps. The free energy relationship is given by a general equation (6).

$$\log k'_n = m \log \beta_{lmn} + C \quad (6)$$

$m(= -1)$ is the slope and $C(= k_r \beta_5)$ is the intercept.

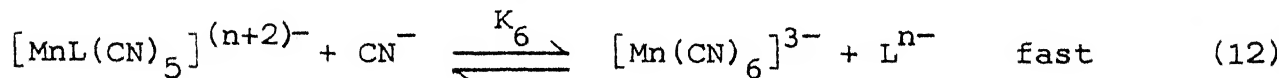
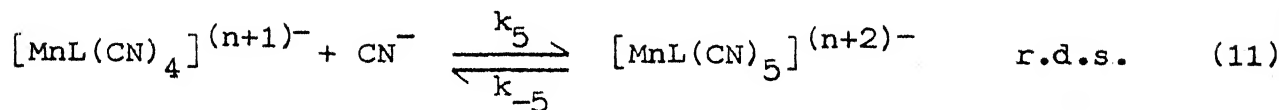
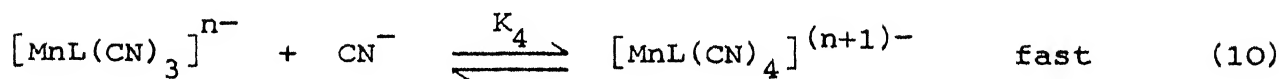
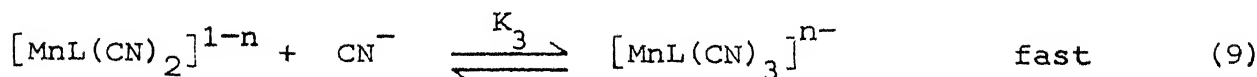
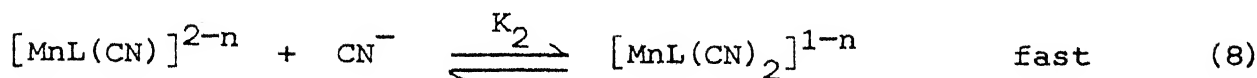
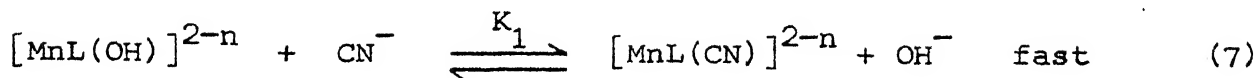
Chapter III contains results and conclusions of the investigations on the ligand substitution reactions of aminocarboxylato-manganate(III) by the cyanide ions. In this study $\text{L}^{n-} = \text{EDTA}^{4-}$ (ethylenediaminetetraacetate anion) HEDTA^{3-} (hydroxyethylethylenediaminetriacetate anion) and CYDTA^{4-} (1,2-diaminocyclohexanetetra-

acetate anion). The reactions between $MnL(OH)$ and CN^- have been followed spectrophotometrically under pseudo-first-order conditions. The reaction conditions are given below:

L^{n-}	Temp. $^{\circ}C$	pH	Ionic strength (I), M($NaClO_4$)	λ_{max} (nm), $\epsilon, M^{-1}cm^{-1}$
EDTA ⁴⁻	25 ± 0.1	10.0 ± 0.02	0.1	325, λ_{max} of $[Mn(CN)_6]^{3-}$, $\epsilon = 3 \times 10^3$
HEDTA ³⁻	25 ± 0.1	9.5 ± 0.02	0.1	449, λ_{max} of $[MnHEDTA(OH)]^{1-}$, $\epsilon = 312$
CYDTA ⁴⁻	25 ± 0.1	10.5 ± 0.02	0.25	448, λ_{max} of $[MnCYDTA(OH)]^{2-}$, $\epsilon = 329$

Here also a variable order dependence in cyanide for forward reaction (in case of EDTA) and first order dependence (in case of HEDTA and CYDTA), and in inverse-first-order dependence in cyanide for reverse reaction in all the three cases, lead to a six step mechanistic pathway in which the fifth step is rate-determining.

The stepwise mechanism can be written down from equation (7-12) as:

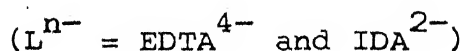
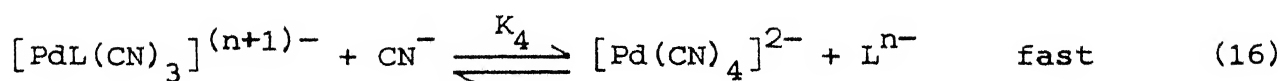
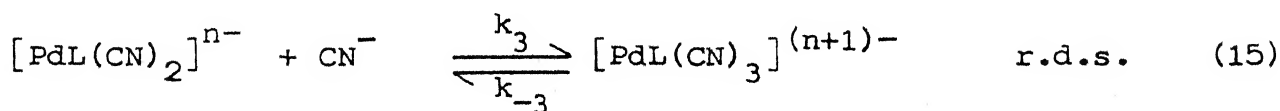
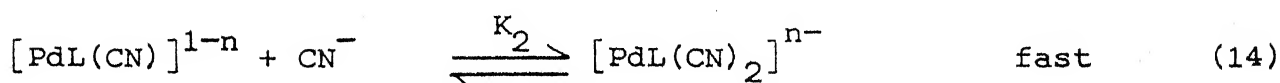
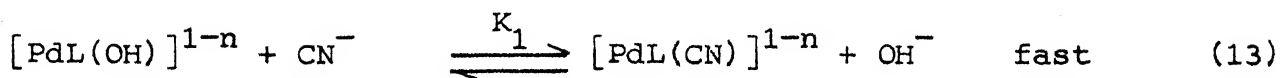


The mechanism proposed by us is at variance with a mechanism proposed earlier by some previous workers for $\text{MnCYDTA}(\text{OH})-\text{CN}^-$ reaction and arguments have been advanced for refutation of their mechanism and in support of the mechanism proposed by us. To the best of our knowledge this is the first comprehensive study of the ligand substitution reactions on $\text{Mn}(\text{III})$ centre.

The subject matter of chapter IV is the study of ligand substitution reactions of square planar complexes viz. $\text{PdEDTA}(\text{OH})$ and PdIDA by cyanide ions. The reactions have been investigated by stopped flow technique at 350 nm (λ_{max} of $\text{PdEDTA}(\text{OH})$ and

330 nm (λ_{max} of PdIDA) at pH = 11.5 and 11.0 respectively, temp. = $25 \pm 0.1^\circ\text{C}$ and $I = 0.1\text{M}$ (NaClO_4). The forward reaction exhibited zero order dependence in cyanide at low cyanide concentration and one at high cyanide concentration in case of PdEDTA(OH) and only first order dependence in cyanide in case of PdIDA reaction. The reverse reaction, which is thermodynamically very unfavourable, could not be forced even in presence of very large excess of ligands inspite of repeated efforts.

Activation parameters (both for zero and first order dependence conditions) have been determined. The effect of pH and ionic strength have also been investigated, interpreted and used in support of the proposed tentative mechanism given from equations (13-16) where the third step is the rate-determining one.



It may be stated, however, that in absence of any observable reverse reaction, an unequivocal mechanism for this reaction can not be proposed and we have relied on our intuition and experience on other systems and ventured to propose a tentative reaction scheme only.

An interesting sideline of the work is an investigation of the oxidation of polyalkylenepolyamines by hexacyanoferrate(III). The results and conclusions are given in chapter V. The polyalkylenepolyamines (P) chosen for these reactions are dien (diethylenetriamine), trien (triethylenetetramine) and tet (tetraethylenepentaamine). The reaction conditions are: $\text{pH} = 10.5 \pm 0.02$, $I = 0.1\text{M}(\text{KNO}_3)$ and $\text{temp.} = 25 \pm 0.1^\circ\text{C}$ and 420 nm (λ_{max} of $[\text{Fe}(\text{CN})_6]^{3-}$, $\epsilon = 1020\text{ M}^{-1}\text{cm}^{-1}$).

An analysis of the effect of pH on the rate of reaction gave resolved rate constants due to reactions of $[\text{Fe}(\text{CN})_6]^{3-}$ with P , HP^+ and H_2P^{2+} , the latter two being protonated forms of polyalkylenepolyamines. Activation parameters lend further support to the proposed mechanism whose basic feature is the one electron oxidation of the polyalkylenepolyamines by hexacyanoferrate(III).

The thesis contains figures, tables and references to related work wherever necessary.

PUBLICATIONS

Part of the work has been published/communicated in National/International Scientific Journals, listed below.

1. Kinetics and Mechanism of Pentacyanohydroxoferrate(III) formation from FeL Complexes (L = Triethylenetetra-aminehexaacetic acid and 2-hydroxy-1,3-diaminopropane-tetraacetic acid),
Pratima Mishra, Radhey M. Naik and Prem C. Nigam, Inorg. Chim. Acta, 1987, 127, 71.
2. Kinetics and Mechanism of Pentacyanohydroxoferrate(III) formation from $[\text{FeL}(\text{OH})_2]^-$ complex, (L=N-(2-hydroxyethyl)-iminodiacetate anion),
Pratima Mishra and Prem C. Nigam, Transition Met. Chem., 1987, 12, 445.
3. Reaction of ethylenediaminetetraacetatomanganate(III) anion with cyanide ion,
Pratima Mishra, Radhey M. Naik and Prem C. Nigam, Transition Met. Chem., 1987, 12, 571.
4. Kinetics of Oxidation of Triethylenetetraamine by Hexacyanoferrate(III),
Pratima Mishra and Prem C. Nigam, Indian J. Chem., 1988, 27A, 783.
5. Kinetics and Mechanism of reaction between ethylenediaminetetraacetatomanganate(III) and cyanide ion,
Pratima Mishra, Radhey M. Naik and P.C. Nigam, Transition Met. Chem., 1988, 000.
6. Kinetics and Mechanism of reaction between Aminopolycarboxylatomanganate(III) complexes and cyanide ion,
Pratima Mishra and Prem C. Nigam, Inorg. Chem., 1988 (communicated).

LIST OF ABBREVIATIONS

Acac	Acetylacetonate
bipy	2,2'-bipyridyl
Bu ₃ N	Tributylamine
CN ⁻	Cyanide ion
3-CN-py	3-cyanopyridine
Diamper	1,3-diamino-2-methylenepropane
Dien	Diethylenetriamine
DMF	N,N'-Dimethylformamide
DMSO	Dimethyl sulfoxide
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EGTA	(Ethylenedioxy)diethylenedinitrilotetraacetic acid
en	Ethylenediamine
Et ₄ dien	N,N,N',N'-tetraethyldiethylenetriamine
Et ₂ NH	Diethylamine
Et ₃ N	Triethylamine
HEDTA	Hydroxyethylethylenediaminetriacetic acid
HIDA	(Hydroxyethyl)iminodiacetic acid
Hipt	4-Isopropyltropolone

MeCN	Acetonitrile
3,5-Me ₂ -py	3,5-dimethylpyridine
Mpt	1-methylpyridine-2-thion
N ₃ ⁻	Azide ion
NTA	Nitrilotriacetic acid
OHP	4,7-dihydroxy,1,10-phenanthroline
-ONPh	Nitrosobenzene
Par	4-(2-pyridylazo) resorcinol
PDTA	Propylenediaminetetraacetic acid
Phen	1,10'-phenanthroline
PrNH ₂	Propylamine
Sal	Salicylate ion
Salen	N,N-ethylene bis(salicylideneaminato)
Terpy	Terpyridyl
Tet	Tetraethylenepentaamine
TPP	Tetraphenylprophine
Trien	Triethylenetetraamine
TTHA	Triethylenetetraaminehexaacetic acid

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CHAPTER I

INTRODUCTION

In the context of coordination chemistry 'substitution' implies replacement of an atom or a functional group present in a molecule by another atom or a functional group. The reactions involving replacement of a ligand constitute an important class of reactions called 'ligand substitution reactions' which are of great utility in analytical and synthetic chemistry. As judged by published work, maximum attention has been given to studies on kinetics and mechanisms of the octahedral and to a lesser extent on square planar or other geometries.

Many of the early kinetic studies on substitution are concerned with the inert Co(II) complexes, which Werner had so well characterized and which usually undergo reactions at conveniently measured rates. Taube's review¹ in 1952 drew attention to the wider world of 'labile' octahedral complexes of transition metals and to reactions which are complete within mixing time. Substitution reactions occur with a very wide range of rates. Some

proceed almost instantaneously, others occur at so low rates that for all practical purposes the reactions do not seem to take place. Thus the words 'labile' and 'inert' came into use in coordination chemistry. The most labile aquo ions are those of the alkali and alkaline earth metals and those of Cd^{2+} , Hg^{2+} , Cu^{2+} and Cr^{2+} . For these ions, observed first order rate constants exceed 10^8 sec^{-1} , whereas in inert complexes e.g. $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Rh}(\text{H}_2\text{O})_6^{3+}$, the substitution proceeds at rates with half lives of several days. A typical example of a slow reaction is the exchange of NH_3 in aqueous solutions with $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ions (no change in 162 days).³

The kinetics and mechanism of reactions involving displacement of polyamines^{4,5} and polyaminocarboxylates⁶⁻¹³ coordinated to $\text{Ni}(\text{II})$ by the monodentate cyanide ions have been studied extensively. Work has also been reported on ligand exchange kinetics and mechanisms of reactions of mono-, bis- and binuclear complexes of $\text{Ni}(\text{II})$,⁶⁻¹⁵ $\text{Fe}(\text{II})$ ¹⁶ and $\text{Fe}(\text{III})$ ¹⁷⁻²⁶ with cyanide ions. Excellent reviews on the substitution of the octahedral $\text{Ni}(\text{II})$ ²⁷ and $\text{Fe}(\text{III})$ ²⁸ complexes have been attempted by workers from our laboratory. Ligand displacement kinetics of $\text{Mn}(\text{III})$ complexes have, however, received little attention.^{29,30} Recently comprehensive studies on the displacement of aminocarboxylates complexed to $\text{Mn}(\text{III})$ by cyanide ions have been carried out by us.³¹⁻³³

Substitution reactions of square planar complexes having low spin d^8 configuration have been studied in some depth.^{34,35} Investigations on square planar complexes e.g. Rh(I), Ir(I), Pd(II), Cu(II) and Au(II) have been, rather, limited because of the difficulties arising from the measurement of their fast reaction rates. But this has been made possible later due to the development of techniques like continuous-flow, stopped-flow, pressure-jump and temperature-jump methods.³⁶ In recent years kinetic study of both monodentate and multidentate ligand exchange reactions on Pd(II) centre have been carried out in our laboratory.^{37,38}

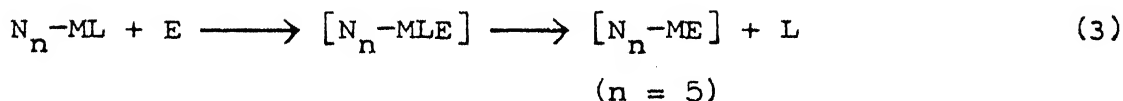
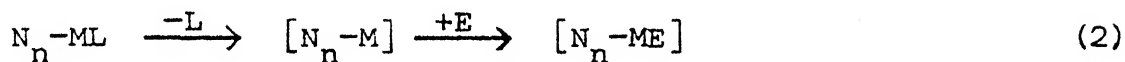
I.2 Mechanisms

Study of substitution mechanisms has occupied many workers for a long time and continues to be an active area of research.³⁹⁻⁴⁴ A general mechanism for the ligand exchange on octahedral and square planar complexes can be given by equation (1):



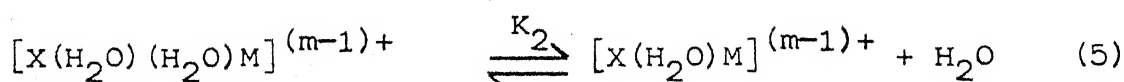
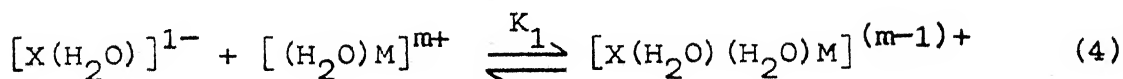
where $n = 5$ and 3 for octahedral and square planar complexes respectively, N = a 'non-hindered' ligand, L is the leaving ligand and E is the entering ligand. In the substitution process the oxidation number of the metal generally remains unchanged.

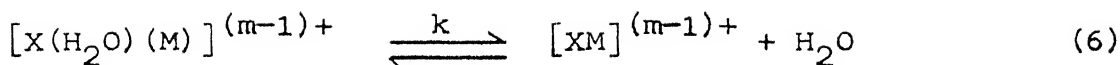
Octahedral complexes conceivably can react via either a dissociative (D or S_N1) mechanism or an associative (A or S_N2) mechanism represented by equations (2) and (3) respectively.



In the first case (equation 2) the leaving ligand L is lost in the first step, producing an intermediate of reduced coordination number. In the second case (equation 3) the entering group adds in the first step producing an intermediate of increased coordination number. A third alternative is an interchange mechanism (I) in which first an outer sphere complex is formed and then the leaving group moves from the inner to the outer coordination sphere, and simultaneously the entering group moves from the outer to the inner coordination sphere.

An illustration of an interchange mechanism is provided by the replacement of a water molecule bound to a metal ion by an anionic ligand X^{n-} . The reactions taking place can be represented by eqns. (4-6).





The first two steps (eqns. 4 and 5) usually correspond to the fast diffusion-controlled process, the equilibrium constants are small, and there is hardly any independent method to measure them directly. So no kinetically detectable intermediates are formed under this class.

A reaction proceeding through interchange mechanism may have a variety of transition states, but two well defined types will be those resembling the transition states of A and D reactions. Thus the interchange is subdivided into an associative activation or interchange (I_a), where the reaction rate is more sensitive to variation of the entering group rather than to variation of the leaving group and a dissociative activation or interchange (I_d), where the reaction rate is much more sensitive to variation of the leaving group than that of entering group. The a-d dichotomy appears to be the only convenient subdivision of interchange process that is necessary for a comprehensive discussion of ligand substitutions. So the simplest notation designating both stoichiometric and intimate mechanism are D, Id, Ia and A.

Substitution on square planar complexes usually occurs through an associative (A or S_N2) mechanism represented by eqn. (3), where $n = 3$, involving a 5-coordinated intermediate.

I.3 Literature Survey

A brief literature survey on substitution reactions of octahedral and square planar complexes is being presented giving particular emphasis on Fe(III), Mn(III) and Pd(II) complexes. Substitution reactions of other metal ions are discussed in appropriate places for comparison, wherever necessary. For the sake of convenience the various reactions have been put under different categories.

I.3.1 Formation reactions

The formation of metal complexes takes place through solvent exchange where usually water acts as a solvent. Recently an excellent review on the formation reactions of Fe(III) complexes has been attempted.²⁸ A dissociative D or I_d mechanism for the formation of labile complexes of divalent cations is well established.⁴⁵ Hayman and Tapuchi,⁴⁶ who have studied the formation kinetics of Fe(III) complexes, showed that these systems also follow a dissociative pathway whereas formation of trivalent cation complexes proceed by an associative mechanism.^{47,48} In recent years, one of the diagnostic tests, that is now being widely used for elucidating the mechanism, is the volume of activation (ΔV^\ddagger).⁴⁹⁻⁵³ The values of activation volumes for complexation of Fe(III) ions are listed in Table I.1. The values are consistently positive for $\text{Fe}(\text{OH})^{2+}$ and

Table I.1. Activation volumes^a for complexation of Iron(III) ions.

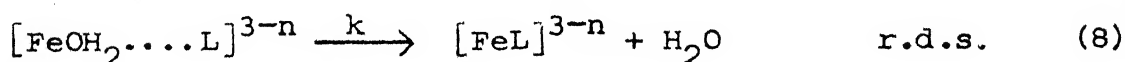
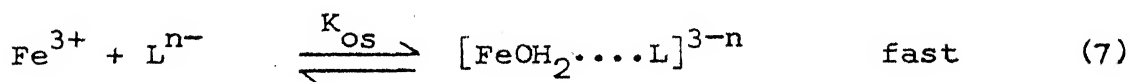
Ligand	ΔV^\ddagger (cm ³ mol ⁻¹)		Ref.
	Fe ³⁺	Fe(OH) ²⁺	
Cl ⁻	-4.5 \pm 1.1	7.8 \pm 1.0	54
Br ⁻	-8 \pm 4	-	55
H ₂ O	-5.4 \pm 0.4	7.8 \pm 0.2	56
NCS ⁻	-12	8.8	57
NCS ⁻	\sim 0	7.1 \pm 1.0	58
Hipt	-8.7 \pm 0.8	4.1 \pm 0.6	59

^adisregarding any initial ion-pairing.

negative for Fe^{3+} pointing to a dissociative and associative mechanism respectively.

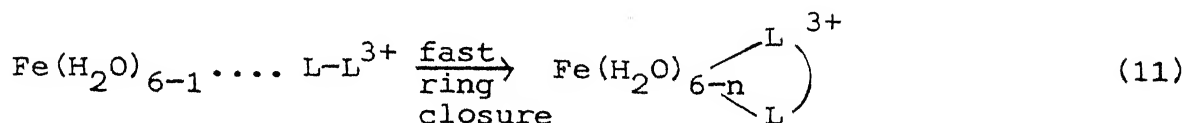
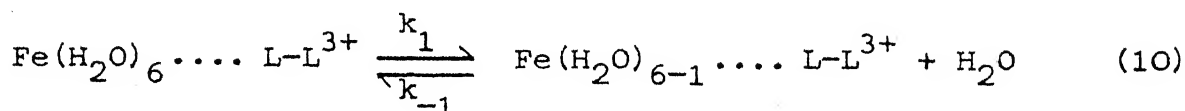
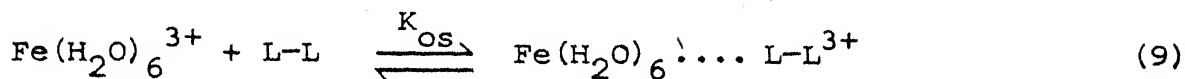
Formation of Fe(III) complexes involving simple ligands viz. Cl^- , Br^- , SCN^- and SO_4^{2-} have been investigated by many workers. This involves reaction with either Fe^{3+} or $\text{Fe}(\text{OH})^{2+}$ ions. The main difficulty in the study of formation reactions of Fe(III) complexes arises due to hydrolysis of the free metal ions Fe^{3+} or easy dimerization of $\text{Fe}(\text{OH})^{2+}$. The rate of formation of a series of Fe(III) complexes from Fe^{3+} lie in the range $1-10^2 \text{ M}^{-1} \text{ s}^{-1}$ whereas for $\text{Fe}(\text{OH})^{2+}$ are larger and lie in the range $1 \times 10^2 - 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Specific complex formation rate constants for $\text{Fe}(\text{OH})^{2+}$ -ligand (monodentate or multidentate) reactions have been compiled and reported earlier.²⁸ The results indicate that the substitution of water molecule in the inner coordination sphere of the metal ions constitutes the rate-determining step for the complex formation reactions.

Eigen and Tamm^{69,70} have proposed the mechanism for complex formation, represented by the following steps:



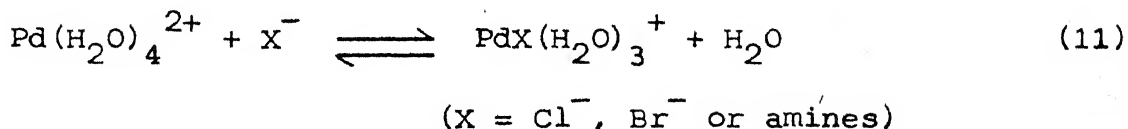
K_{os} is equilibrium constant for the formation of outer-sphere complex, k is rate constant for formation of the complex and Fe^{3+} may be $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ or $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$.

The mechanism for formation of complexes from unidentate ligands can be extended to the formation of n-dentate ligands as given in eqns. (9-11).



where L-L represents an n-dentate ligand.

References to the studies of formation kinetics of Mn(III) complexes are scarce. But some studies have been reported on formation reactions of Pd(II) complexes. For example, the formation kinetics of Pd(II) complexes has been carried out for ligands viz., Cl^- , Br^- ^{71,134} and amines.⁷² Substitution reactions of Pd^{2+} cation indeed provide a uniquely interesting example of complex formation from a square planar aquo-cation $\text{Pd}(\text{H}_2\text{O})_4^{2+}$.



Rate constants and activation parameters for X (X = Cl^- or Br^-) are given in Table I.2. Eldik and Mahal⁷³ have studied the

Table I.2. Rate constants, activation enthalpies and activation entropies at 25°C for substitution reactions of palladium(II) complexes⁷¹ (aqua ligands excluded).

Process	$k,$ M^{-1}, s^{-1}	ΔH^\ddagger $kcal\ mol^{-1}$	ΔS^\ddagger $cal\ K^{-1}mol^{-1}$
$Pd^{2+} + Cl^- \longrightarrow PdCl^+$	1.38×10^4	10 ± 2	-6 ± 6
$Pd^{2+} + Br^- \longrightarrow PdBr^+$	9.2×10^4	10 ± 1	-3 ± 3
$PdCl_3^- + Cl^- \longrightarrow PdCl_4^{2-}$	1.8×10^2	10 ± 1	-15 ± 3
$PdBr_3^- + Br^- \longrightarrow PdBr_4^{2-}$	3.0×10^3	8 ± 1	-17 ± 3

kinetics of formation of carbonate complexes of Pd(II) and found that these complexes are formed via anation of aquo complexes, $\text{Pd}(\text{H}_2\text{O})_4^{2+}$. Elding et al. have studied the kinetics of complex formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and L (L=DMSO⁷⁴ and MeCN⁷⁵). In all these cases an associative mode of activation takes place. Contrary to this, in the reactions of Ni(II) ions a dissociative mechanism has been established. In general, square planar complexes of Pd(II) and Ni(II) are much more labile than that of analogous Pt(II) complexes. The relative reactivities of analogous Ni(II), Pd(II) and Pt(II) complexes are approximately $10^{7-8}:10^{5-6}:1$.⁷⁶

I.3.2 Solvent exchange reactions

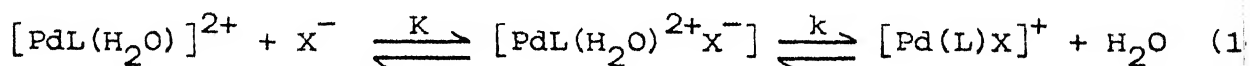
The study of substitution on complexes in aqueous solutions does not always resolve unambiguously the problem of reaction mechanism because of the dual role of water as a reagent and a solvent. Comparison of solvent-exchange reaction rates has been used as a good criterion for elucidation of the mechanisms of substitution reactions.⁴³ Kong and John⁷⁷ have studied the solvent effects on A (or $\text{S}_{\text{N}}2$) reactions. More recently, information has been available for the octahedral first row transition metal ions which leads to the inference that the mechanisms for solvent exchange and ligand substitution are similar.⁷⁸ A solvent exchange reaction showing

Table I.3. Kinetic parameters of the solvent exchange reactions of Fe(III) complexes at 25°C.

Complexes	Solvent	k_1 , s^{-1}	ΔH^\ddagger $kcal\ mol^{-1}$	ΔS^\ddagger $cal\ K^{-1}\ mol^{-1}$	Ref.
$[Fe(acac)_3]$	Hacac	3.3×10^{-3}	14.4 ± 0.9	-22.3	91
$[Fe(H_2O)_6]^{3+}$	H ₂ O	150	-	-	92
$[Fe(dmf)_6]^{3+}$	DMF	33	12.5 ± 1.5	-10 \pm 5	92
$[Fe(dmf)_6]^{3+}$	DMF	61	10.1 ± 1.0	-16.5 \pm 3.0	84
$[Fe(DMSO)_3]^{3+}$	DMSO	50	10 \pm 2	-11 \pm 4	82

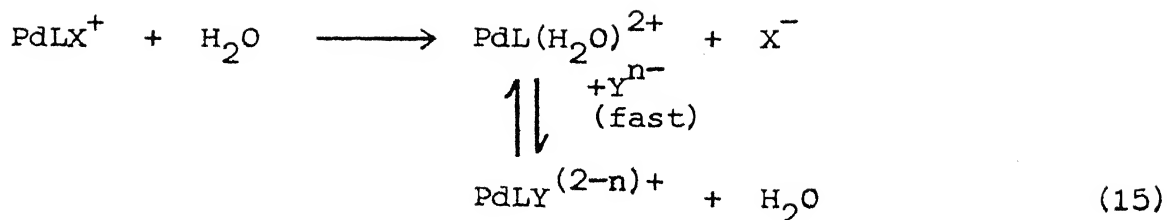
(${}^5B_{1g} \rightarrow {}^5A_{1g}$) in many of these complexes is very sensitive to the solvent interaction.²⁹ A low energy band of $MnL_2(H_2O)_2$ species is seen in pyridine, where the coordinated water, presumably, is replaced by the amine (L = β -diketone, acetate and tropolonate). Although studies on Mn(III) β -ketoenol complexes have been carried out in different organic solvents, but solvent exchange is seen only in pyridine. Kinetic studies of many reactions of Mn(III) complexes have been hampered by the instability of the aquomanganese(III) ion.^{94,95}

Solvent exchange kinetics of Pd(II) complexes have been investigated by many workers. Solvent effects on leaving group in the reactions of neutral and cationic Pd(II) complexes have also been studied.⁹⁶ A general mechanism for solvent exchange of Pd(II) complexes involving ion-pairing⁹⁷ has been represented as:



The mechanism of this reactions has been explained by solvent assisted dissociative mechanism.

The reaction mechanisms of some pseudo-octahedral complexes have been studied⁴³ and are given in eqn.(15).



where L = Et₄dien, MeEt₄dien and Me₅dien. For all these complexes, a solvent-assisted associative mechanism has been proposed. The sequence for interchange of X and Y has been shown to be feasible by demonstrating the rapidity of the second step. Rate constants for the reaction of PdL(H₂O)²⁺ (L = Et₄dien) with different ligands Yⁿ⁻ have been compiled in Table I.4.

The rate of reaction of halides with Pd(Et₄dien)X⁺ (X = Cl⁻, Br⁻ and I⁻) complexes have been investigated as a function of temperature in different solvents.^{98,99} The activation parameters show that for reactions in protic solvents, a dissociative mechanism with leaving group solvation is probable. Kinetic data for all the three cases (X = Cl⁻, Br⁻ and I⁻) have been reported by Roulet and Gray.¹⁰⁰ In protic solvents the reactivity decreases as X is varied in the order Cl⁻ > Br⁻ > I⁻. Evidence for a dual mechanism in the reaction of [Pd(Et₄dien)X]⁺ complexes has been given by Palmer and Kelm.¹⁰¹ The rates of substitution of X in [Pd(dien)X]NO₃ (X = Cl⁻, Br⁻, I⁻, N₃⁻, SCN⁻ and NO₂) by PrNH₂ and (NH₂)₂CS have been studied.⁹⁶ The results show that both the rate and the equilibrium constants vary on going from protic to dipolar aprotic solvents and the lability sequence of the leaving group depends on the nature of

Table I.4. Rate constants for the reactions of $\text{Pd}(\text{Et}_4\text{dien})\text{H}_2\text{O}^{2+}$ with different ligands Y^{n-} at 25°C .⁹⁸

Y^{n-}	$k, \text{M}^{-1}\text{s}^{-1}$
$\text{S}_2\text{O}_3^{2-}$	1.8×10^3
HSO_3^-	5.1×10^2
SCN^-	72
NO_2^-	13
Cl^-	7.4
Br^-	6.0
I^-	4.5
CH_3COO^-	2.2
$\text{SC}(\text{NH}_2)_2$	1.4

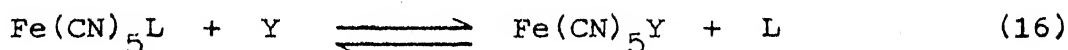
the substrate and the solvent. Similarly substitution reactions of 1,3-[PdPy₂Cl₂] in different solvents have been studied and kinetic data have been reported.¹⁰²

I.3.3 Ligand exchange reactions

I.3.3.1 Monodentate or Multidentate by Monodentate

These reactions involve the exchange between a monodentate or multidentate ligand complexed to a metal centre and another monodentate ligand. Reactions in which water acts as a solvent as well as a ligand, have been discussed earlier (vide infra).

Substitution reactions of pentacyanoferrate(II)/(III) follow the overall reaction (eqn. 16).



where L and Y are monodentate ligands. Kinetics of substitution reactions of $[\text{Fe(CN)}_5\text{L}]^{3-}$ (L = NO, 3,5-Me₂-Py, -ONPh, -SO₃, Py and 3-CN-Py etc.) have been studied recently and shown to follow a dissociative mechanism. The kinetic parameters have been compiled and reported before.¹⁰³ Ali et al.¹⁰⁴ have studied the substitution reactions of 4-cyanopyridine complexes $[\text{Fe(CN)}_5\text{4CN-Py}]$ where 4-CN-Py acts as the substituent, and found that these reactions also follow a dissociative path. Stochel et al.¹⁰⁵ have

studied the kinetics and mechanism of acid-catalyzed aquation and base hydrolysis of $\text{Fe}(\text{CN})_5\text{NO}$ in aqueous media. However, number of reported replacement reactions of unidentate ligands coordinated to $\text{Fe}(\text{III})$ by other unidentate ligands are limited.¹⁰⁶

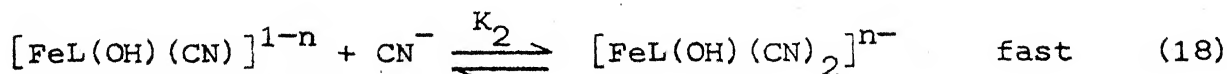
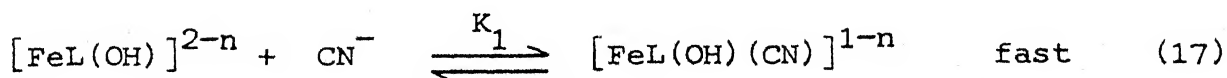
The cyanide ion is a potential unidentate ligand having a capability of displacing multidentate ligands viz. macrocyclic ligands, polyamines, polyaminocarboxylates and thioligands like dithiocarbamates and dithiophosphates from their metal complexes. The reactions involving NiL complexes (L = macrocyclic ligands,¹⁰⁷⁻¹¹ polyamines^{4,5} and polyaminocarboxylates⁶⁻¹³) have been studied extensively by many workers. For the past few years Nigam et al. have been investigating the substitution reactions of aminocarboxylates complexed to $\text{Fe}(\text{III})$ ^{17-24,28} by cyanide ions.

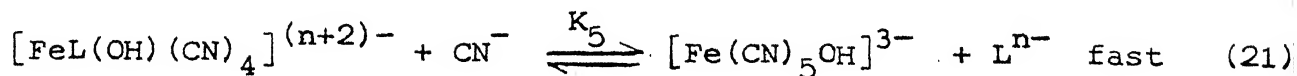
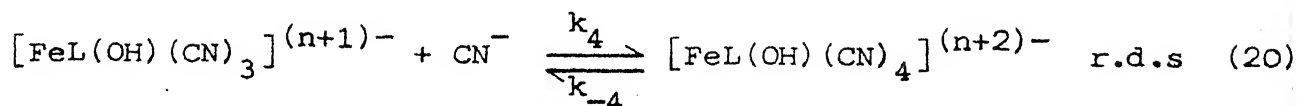
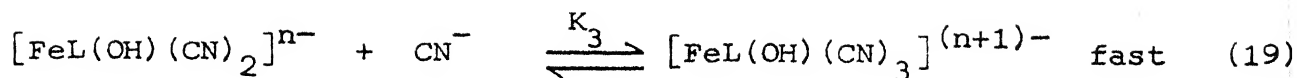
Reactions of cyanide ions with cationic complexes $\text{Fe}(\text{L-L})_3^{2+}$ (L-L = 1,10-phenanthroline¹¹¹ or a substituted phen,^{112,113} Schiff's base,¹¹⁴ bipy,¹¹⁵⁻¹¹⁹ substituted bipy¹²⁰ and terpy^{121,122} or diimine¹²³) proceed through formation of mixed complexes of the type $\text{Fe}(\text{L-L})_2(\text{CN})_2$. The reactions of bis complexes of $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ with $\text{Par}^{16,26}$ (Par = 4-(2-pyridylazo)resorcinol) with cyanide ions too follow the same path way, forming mixed ligand complexes, where only one of the ligands is displaced even in presence of large excess of cyanide.

Vu and Stanbury¹²⁴ have investigated the substitution reaction of $\text{Fe}(\text{OHP})_3$ with cyanide (OHP = 4,7-dihydroxy, 1,10-phenanthroline) and found that this reaction has the same rate law as the redox reaction with HO_2^- which is interpreted to mean that the loss of ligand takes place in the rate-determining step. Theoretical study of kinetics of substitution of CN^- or OH^- in $\text{Fe}(\text{II})$ phenanthroline complexes in micellar media has been carried out by Orlega and Rodenos.¹²⁵

For the past few years we have been investigating the kinetics and mechanism of displacement of aminocarboxylates complexed to $\text{Fe}(\text{III})$ and of the less studied $\text{Mn}(\text{III})$ and proposed a multistep mechanism for both reactions where the rate-determining step is the step preceding the last one. The reactions of $[\text{MLOH}]^{2-n}$ ($\text{M}=\text{Fe}(\text{III}), \text{Mn}(\text{III})$ and L = aminocarboxylates) complexes and cyanide ions have been shown to involve the formation of mixed ligand intermediates of the type $[\text{ML}(\text{OH})(\text{CN})_x]^{2-n-x}$ in multistep reaction sequences proposed by us.

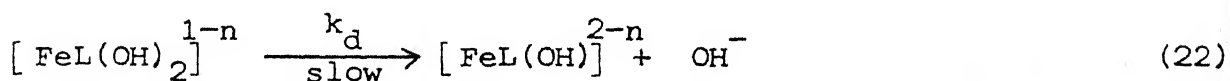
Further, the $\text{FeL}(\text{OH})-\text{CN}^-$ reaction takes place in three stages. The mechanism for the first stage i.e. the formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ from $[\text{FeL}(\text{OH})]^{2-n}$ complexes is given from eqns.17-21





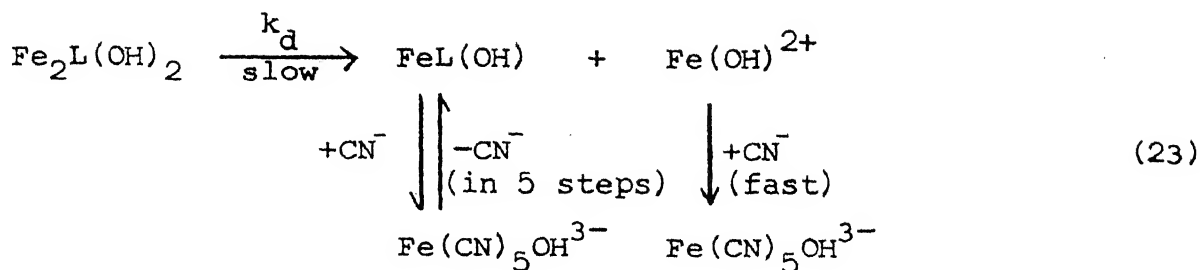
where $\text{L} = \text{HPDTA}^{4-}$,²³ HIDA^{2-} ,²⁴ EDTA^{4-} ,^{17,18} HEDTA^{3-} , DTPA^{5-} ,¹⁹⁻²¹ PDTA^{4-} ²² and TTHA^{6-} .²³ The second stage of the reaction is the conversion of $\text{Fe}(\text{CN})_5\text{OH}^{3-}$ to $\text{Fe}(\text{CN})_6^{3-}$ by the reaction with cyanide ions, present in excess.²⁸ The third stage is the reduction of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ by the ligand, released during the first stage.

The $\text{Fe}(\text{III})$ complexes with $\text{L}^{23,24}$ ($\text{L} = \text{HIDA}$ and TTHA) are present as dihydroxy species at higher pH. In their reaction with cyanide, the slow loss of one hydroxy group precedes the exchange with cyanide as given in eqn.(22).



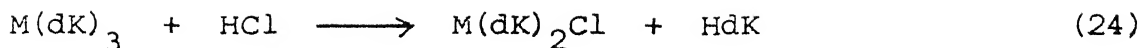
This is followed by the same sequence of steps as given in eqns. (17-21). The reactions of binuclear complexes of $\text{Fe}(\text{III})$ with cyanide have also been studied.²⁵ The first step in these reactions is the loss of $\text{Fe}(\text{OH})^{2+}$ in a slow step according to eqn.(23) followed

by the same sequence as in the case of mononuclear complexes (eqns. 17-21).



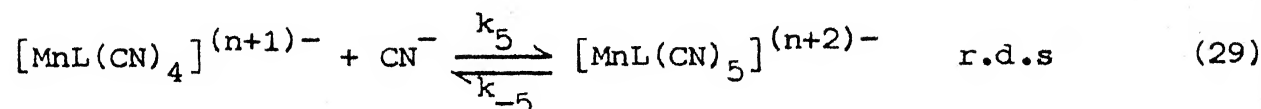
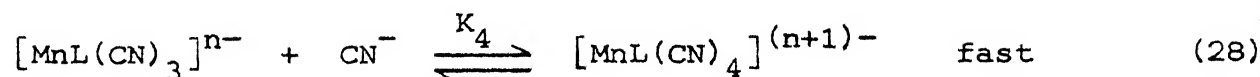
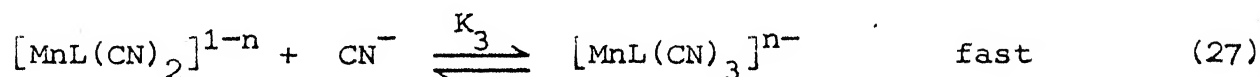
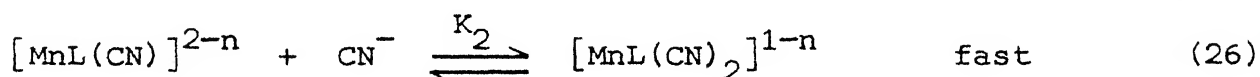
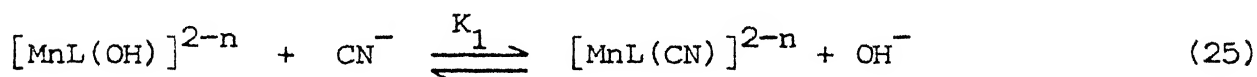
Few substitution reactions of Mn(III) complexes have been investigated. Reactions of MnCl_3 with 2,2'-bipyridyl and o-phenanthroline result in the formation of complexes,¹²⁶ $[\text{MnL}]\text{Cl}_3$ (L = bipy and phen), from which the chloride could be substituted by other ions. Substitution reaction between MnCl_3 and acetylacetone give complexes viz. $\text{Mn}(\text{acac})\text{Cl}_2$ and $\text{Mn}(\text{acac})_2\text{Cl}$. But for both reactions kinetic studies have not been reported yet.¹²⁶

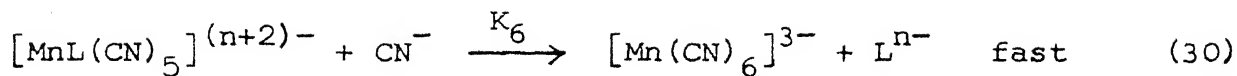
Edmund and Waldemar¹²⁷ have studied the reaction of β -diketone complexes of Mn(III) and Fe(III) with HCl in methanol and showed that the bidentate diketonate ligands are easily replaced by the monodentate chloride ions. The kinetic data show that in the first step one β -diketonate ligand is substituted by chloride ion almost quantitatively in both Mn(III) and Fe(III) complexes.



where $M = Fe(III)$ and $Mn(III)$, dK is the diketonate ligand.

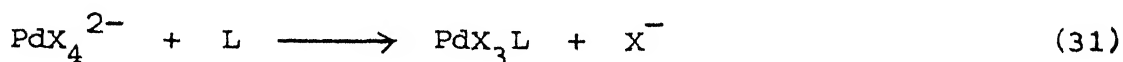
More recently we have carried out investigation on the reaction of $MnL(OH)$ complexes with cyanide ions³¹⁻³³ (L = ethylenediaminetetraacetic acid, EDTA and (hydroxyethyl)ethylenediaminetriacetic acid, HEDTA) and proposed a general six step mechanism for the formation of $[Mn(CN)_6]^{3-}$. We have also undertaken a reinvestigation of the $MnCYDTA(OH)-CN^-$ reaction ($CYDTA^{4-} = 1,2$ -diaminocyclohexanetetraacetate anion), studied earlier by Hamm and Templeton³⁰, and refuted their mechanism. This reaction is also shown to follow the mechanism proposed by us for $EDTA^{4-}$ ^{31,32} and $HEDTA^{3-}$ systems and which is given from eqns. 25-30.





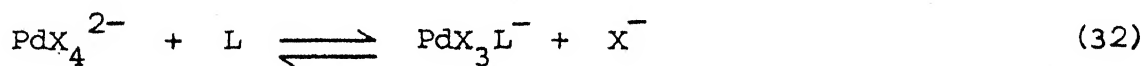
$\text{L} = \text{CYDTA}^{4-}, \text{HEDTA}^{3-} \text{ and } \text{EDTA}^{4-}.$

Ligand exchange kinetics of Pd(II) complexes have been studied by many workers. Cattalini et al.¹²⁸ have carried out the kinetic study on substitution of a chloride ion from PdCl_4^{2-} by an amine in aqueous media. The reaction is represented by eqn. (31).



where $\text{X} = \text{Cl}^-$ and $\text{L} = \text{amines}.$

Second order rate constants for various amines are listed in Table I.5. The reaction rate, which depends on the basicity of amines, is drastically reduced by steric hindrance. The rate constants and activation parameters for the reaction of $[\text{PdCl}_4]^{2-}$ and $[\text{PdBBr}_4]^{2-}$ with thiourea and selenourea and a few other ligands have been reported in Table I.6. A comprehensive study on substitution reactions of Pd(II) halide complexes (eqn. 32) has been carried out by many workers.^{133,134}



$(\text{X} = \text{Cl}^- \text{ or } \text{Br}^- \text{ and } \text{L} = \text{H}_2\text{O})$

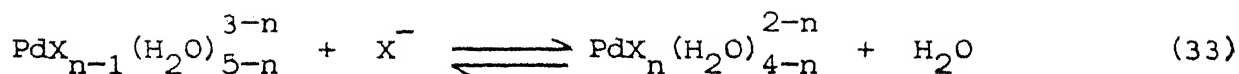
Elding¹³⁵ has studied the substitution reactions of aqua halide complexes, represented by a general eqn. (33).

Table I.5. Second order rate constants for substitution reactions of PdCl_4^{2-} with various amines at 25°C.

Amine	$k_2, \text{M}^{-1}\text{s}^{-1}$	pK
3-chloropyridine	2.5	2.84
4-chloropyridine	360	3.84
Pyridine	780	5.17
3-methylpyridine	1080	5.68
4-methylpyridine	1150	6.02
Morpholine	3300	8.4
2-methylpyridine	38	6.1
2,4-dimethylpyridine	51	6.95
Et_2NH	380	—
2,6-dimethylpyridine	1.4	6.75
2,3,6-trimethylpyridine	1.7	7.25
2,4,6-trimethylpyridine	1.8	7.48

Table I.6. Rate constants along with Activation Parameters for associative nucleophilic attack at $[\text{PdX}_4]^{2-}$ halo-genonions.

Nucleophile L	k_2 , $\text{M}^{-1}\text{s}^{-1}$	ΔH^\ddagger kcal mol^{-1}	ΔS^\ddagger $\text{cal K}^{-1}\text{mol}^{-1}$	Ref.
$[\text{PdCl}_4]^{2-}$				
Ammonia	33	-	-	129
Thiourea	9.1×10^3	6.0	-19.5	130
Selenourea	4.5×10^3	4.4	-26.0	130
Diamper	4.9×10^{-3}	20	+14	131
N,N'-Me ₂ diamper	0.55×10^{-3}	23	+20	131
enH ⁺	296	-	-	132
Me ₂ enH ⁺	153	-	-	132
Me ₄ enH ⁺	14	-	-	132
$[\text{PdBr}_4]^{2-}$				
Thiourea	2.1×10^4	7.3	-19.0	130
Selenourea	9.1×10^4	10.7	- 0.5	130



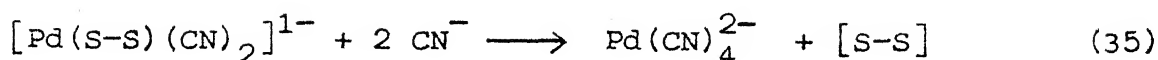
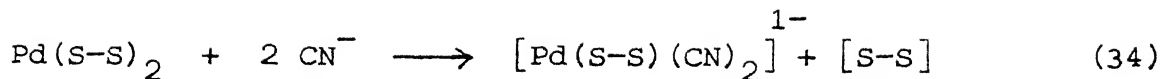
(X = Cl⁻, Br⁻ and n = 2, 3 and 4)

The reaction for n = 1, has already been discussed before (I.3.1). The reactions of [PdX₃L]⁻ and [PdXL₃]⁺ have been found to be very fast owing to the very strong trans effect of both the ligands. Exchange reactions of these ions with tertiary phosphine have been followed by NMR techniques by Louch and Eaton.¹³⁶

Trozzi et al.¹³⁷ have studied the kinetics of substitution reactions of [Pd(terpy)X]⁺ (X = I⁻, Br⁻, Cl⁻, N₃⁻ and NO₂⁻) with Y (Y = (NH₂)₂CS, I⁻, Br⁻, N₃⁻ and Cl⁻). The results can be compared with those of previously studied [Pd(3-NHPd)X]⁺ (3-NHPd = 3-azapentane, 1,5-diamine) complexes. It is reported that the terpy complexes are both more reacting and discriminating between various entering ligands.

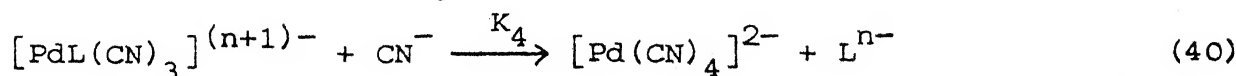
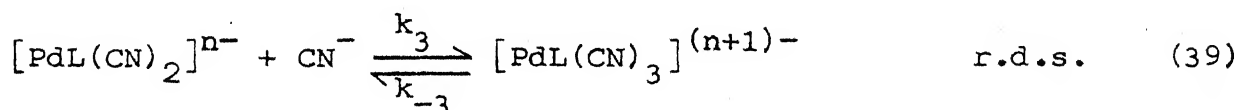
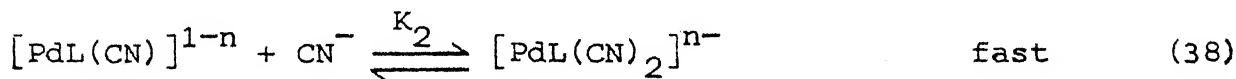
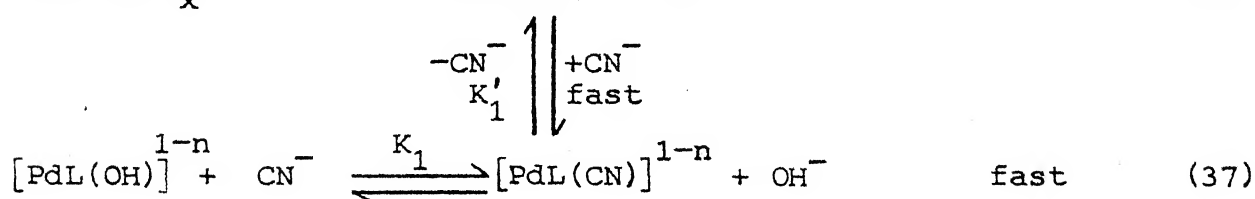
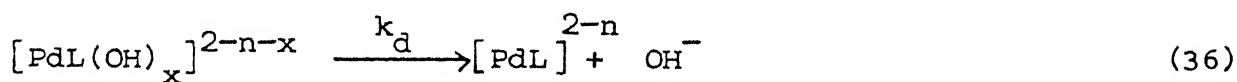
Bromide substitution in the sterically hindered complexes [Pd(Et₄dien)XCN]⁺ and [Pd(MeEt₄dien)XCN]⁺ (X = S or Se) have also been studied and shown to follow a two term rate law.¹³⁸

Hynes and Brannick¹³⁹ have studied the substitution reactions of dithiophosphate and dithiocarbamate complexes of Pd(II) with cyanide ions. A two step mechanism is followed according to eqns. (34-35).



where $[\text{S-S}]^-$ represents the bidentate sulphur ligands.

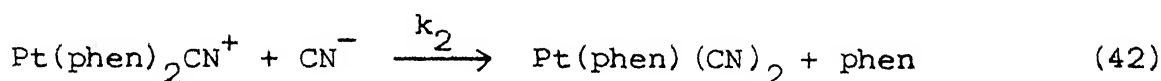
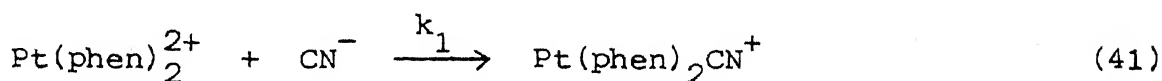
After a long lapse the reaction of Pdpar with cyanide ions, has been studied in our laboratory.³⁷ This reaction follows a four step mechanism where the third step is the rate-determining one. Only recently, we have carried out the reactions of amino-carboxylatopalladate(II) complexes with cyanide ions and proposed a four step mechanism where the third step is the rate determining one. The mechanism is given below (eqns. 36-40).



$\text{L} = \text{Par}^{2-}$, EDTA^{4-} ($x = 1$) and IDA^{2-} ($x = 0$).

In case of PdIDA - CN^- reaction the first step of the reaction mechanism does not occur. It must be admitted, however, that this mechanism proposed for PdL-CN^- ($\text{L} = \text{EDTA}$ and IDA) can not be said to be unequivocal because the reverse reaction does not occur even in presence of excess ligand.

Studies on five coordinated d^8 metal ions viz. the displacement of 1,10-phenanthroline by the reaction of cyano bis(1,10-phen) Pt(II) cation with cyanide have been carried out.¹⁴⁰ A two step mechanism (eqns.41, 42) has been proposed for the same where only one phen is displaced.



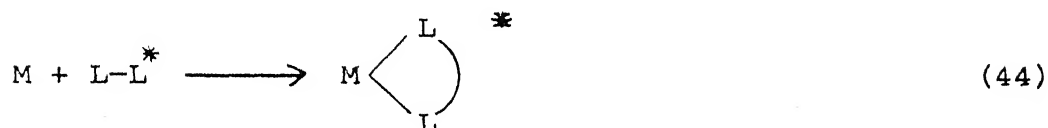
Kinetics of substitution of amines complexed to Pt(II) by cyanide ions have been studied.¹⁴¹ Dickson et al.¹⁴² have reported the reaction involving cyanide displacement from Au(CN)_2^- by 1-methylpyridine-2-thion (mpt). A step-wise substitution of cyanide has been proposed for the same.

I.3.3.2 Multidentate by multidentate

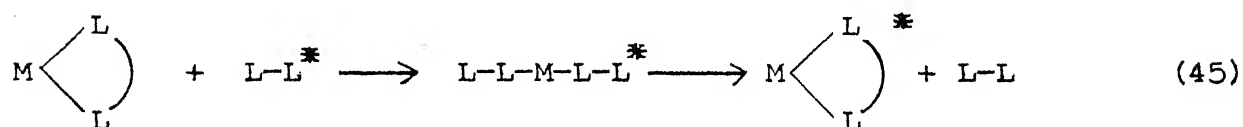
These reactions involve displacement of one multidentate ligand by another from a metal ion complex. The mechanism depends

on the coordinating ability of both the ligands simultaneously and are classified into four types.

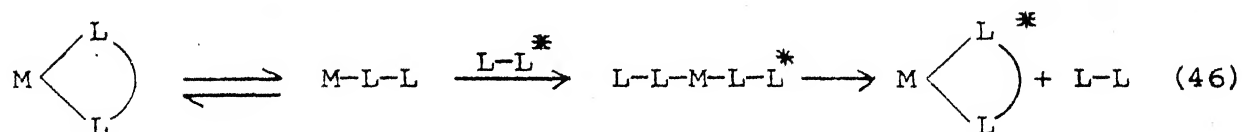
- (i) Complete dissociation of leaving ligand (L-L) from the metal cation (M) before association occurs between M^{n+} and the entering ligand $(L-L)^*$ starts



- (ii) Association of the M^{n+} with entering ligand may occur before dissociation process of leaving ligand completes.

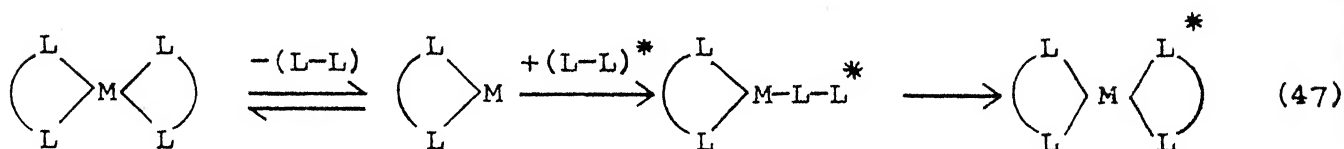


- (iii) A variation of this mechanism is the case of pre-equilibrium partial dissociation of the starting complex.

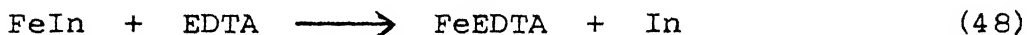


- (iv) Modification of the scheme (iii) where two multi e.g.,

terdentate ligands are replaced by another multi e.g. quinquid or hexadentate ligand. The rate determining step of the overall reaction is the cleavage of any one of the several bonds between metal and the leaving group which must be broken in the course of reaction.



Multidentate ligand exchange kinetics of Fe(III) has received less attention. Reactions of FeL (L = HEDTA and NTA) with Par (4-(2-pyridylazo)resorcinol) have been studied in our laboratory.¹⁴³ Mentasti et al.¹⁴⁴ have investigated the kinetics of displacement of metallochromic indicators (abbrev. In) from their complexes of Fe(III), represented by the eqn. (48).



In = salicylic acid (H_2Sal) or Tiron = 1,2-dihydroxybenzene disulphonic acid (H_2T). The rate constants have been reported and given in Table I.7. Very little is known so far, on the exchange of multidentate ligands on Mn(III) and Pd(II).

Multidentate ligand exchange kinetics of square planar complexes differs from that of octahedral complexes in some respects. There are reports available for Nitrien-L (L = EDTA¹⁴⁵ or HEDTA¹⁴⁶

Table I.7. Rate constants and activation parameters for the reactions of Fe(III) and FeIn with EDTA; temp.=25°C, I = 1.0M, (NaClO₄).¹⁴¹

Reaction	k, 10 ³ , l mol ⁻¹ sec ⁻¹	ΔH^\ddagger kcal mol ⁻¹	ΔS^\ddagger cal mol ⁻¹ deg ⁻¹
FeOH ²⁺ + H ₄ EDTA	30 ± 3	7 ± 1	-15 ± 3
FeOH ²⁺ + H ₃ EDTA ⁻	110 ± 10	6 ± 1	-15 ± 3
FeSal ⁺ + H ₄ EDTA	0.84 ± 0.10	17 ± 2	+ 8 ± 6
FeSal ⁺ + H ₃ EDTA ⁻	14 ± 1	15 ± 1	+ 7 ± 4
FeT ⁺ + H ₄ EDTA	0.58 ± 0.1	17 ± 2	+ 8 ± 6
FeT ⁺ + H ₃ EDTA ⁻	17 ± 1	15 ± 1	+ 9 ± 4

or DTPA¹⁴⁷) and $\text{Ni}(\text{tet})^{2+} - \text{L}$ ($\text{L} = \text{EDTA}^{145}$ or TMDTA^{148} or DTPA^{149} or PDTA^{149}) systems forming mixed ligand intermediates viz. $\text{Ni}(\text{trien})\text{L}$ and $\text{Ni}(\text{tet})\text{L}$ respectively. These intermediates undergo successive unwrapping of trien or tet and increasing coordination with L^{n-} finally giving NiL^{2-n} . The mixed ligand complexes have been sometimes experimentally observed but more often kinetically inferred as reaction intermediates in several other cases of chelate substitution reactions.

Reference to multidentate ligand exchange reactions on metal ions such as $\text{Cd}(\text{II})$,¹⁵⁰⁻¹⁵² $\text{Zn}(\text{II})$,¹⁵³ $\text{Hg}(\text{II})$ ¹⁵⁴ and $\text{Cu}(\text{II})$ ^{153,155,156} are available in literature. A review of the same and their application to analytical chemistry has appeared for systems involving EGTA and PAR¹⁵⁷ (eqn. 49).



Very recently Kido and Hatakeyama have studied the ligand substitution on $\text{Tc}(\text{III})$ centre and found that $\text{Tc}(\text{III})$ has got a lability very close to that of $\text{Cr}(\text{III})$ and undergo I_a ligand substitution.²⁰¹

Reactions of $\text{Pd}(\text{II})$ complexes involving multidentate ligands have been much less studied. Kinetics and mechanism of reactions of PdIDA with L ($\text{L} = \text{ethylenediaminetetraacetic acid}$ and $\text{triethylenetetraminehexaacetic acid}$) have been carried out in our laboratory.³⁶ The reactions of $\text{Pd}(\text{II})$ differ from that of $\text{Fe}(\text{III})$ in some respects. These reactions are of consecutive type in which

a fast formation of the mixed-ligand complex occurs which in turn dissociates into the products releasing the original ligand.

Ligand exchange reactions of Pd (Arsenazo-I) or Pd(Par) with triethylenetetraamine result in the formation of Pd(trien) and Pd(trien)₂ but the kinetics of the same has not yet been investigated.¹⁵⁸ Recently, substitution reaction of Pd(dien) with tris(hydroxymethylaminomethane) in aqueous media has been reported.¹⁵⁹ The reaction of aqueous Pd(1,4,7-Me₃dien)Cl⁺ and Pd(1,1,7,7 Me₄-dien)Cl⁺ with Tris(tris(hydroxymethyl)aminomethane) buffer solutions covering 7 < pH < 9 comprises of two consecutive steps, where both depend on [Cl⁻]. Neither of the rate laws corresponds with the simple two term expression for square planar substitution. A rapid formation of aqua intermediates followed by the formation of a Tris complex, is proposed for the same.

Studies of metal exchange between ligands are,¹⁶⁰⁻¹⁷² by far, very few. Though these reactions can be of considerable theoretical and practical interest but we resist the temptation on discussing them in the present context.

I.4 Applications of ligand substitution reactions

The study of substitution process is important in many ways. Thus rate studies make it possible to define the best conditions for a preparative and an analytical procedure in coordination chemistry,^{173,174} catalysis and inhibition in metalloenzyme-promoted

reactions¹⁷⁵ and transport of metal ions through cell membranes.¹⁷⁶ Besides this, the base hydrolysis of pentaamine Co(III) and many anation reactions have been carried out to study the effect of hydrostatic pressure,¹⁷⁷ ionic strength¹⁷⁸ and ion-pairing¹⁷⁹ on the reaction rates.

I.4.1 Analytical Applications

Many possibilities of analytical interest are provided by study of substitution reactions.^{101,180-192} The presence of many species, particularly metals, in trace amounts is essential for growth and sustenance of life. Determination of these trace species is possible by their catalytic effect on some chosen ligand substitution reactions. For example, Trien¹⁸⁵ and triglycine¹⁸⁶ upto 10^{-5} M concentration level have been determined. One of the most poisonous metals, mercury has been determined upto a limit of 10^{-7} M by its catalytic effect on the substitution rate of cyanide in hexacyanoferrate(II) by p-nitrosodiphenylamine.¹⁹³

Ligand substitution reactions rates have been used for monitoring water quality.¹⁹⁴ Metals in waste water have been determined by their reaction rates. The substitution reactions rates of (1) 1-(2-thiazolylazo)-2-naphthol complex and EDTA, (2) 2-(2-thiazolylazo)-5-dimethylaminophenol complexes and EDTA¹⁹⁵ and (3) 1-(2-pyridylazo)-2-naphthol complexes and EDTA have been utilized in the determination of metals in trace levels. Cu(II) in trace level of 10^{-7} M concentration has been determined by using the method(2).¹⁹⁴

Simultaneous determination of Cd^{2+} and Mn^{2+} in $5 \times 10^{-6} \text{M}$ concentration have been possible by observing the difference in the rates of ligand substitution reaction between 1-(2-pyridylazo)-2-naphthol chelate and EDTA.¹⁹⁵ Similarly binary mixtures of Co(II)-Ni(II) , Cu(II)-Pb(II) , Ni(II)-Fe(III) and Zn(II)-Cd(II) and a mixture of $\text{Co(II)-Ni(II)-Zn(II)-Pb(II)}$ ¹⁹⁶ have been resolved by the differential kinetic method of analysis.¹⁸¹

Components present in binary mixtures of Th, U(VI), Pu(IV) and Np(IV) have been determined by ligand exchange between their complexes and Arsenazo-III.^{197,198} Exchange of EDTA with colored complexes of rare earth metals viz. Dy, Ho and Yb by xylenol orange¹⁹⁹ has been used for the estimation of these metals in ternary mixtures using time as the discriminating variable.

I.4.2 Synthetic Application

Preparations of many complexes are very much difficult by the conventional procedures. A brief discussion on Fe(III) and Pd(II) complexes has been given in I.3.1. More recently, an unstable manganese(III) complex, (p-nitrobenzenethiolate) $[\text{N,N}'\text{-ethylene bis(salicylideneaminato)}]\text{manganese(III)}$ has been prepared by a ligand exchange reaction using Mn(salen)OAc with HSC_6H_5 in MeOH $[\text{salen} = \text{N,N}'\text{-ethylene bis(salicylideneaminato)}]$.²⁰⁰

I.4.3 Determination of stability constants of mixed ligand intermediates produced in multistep reactions

Stability constants of the intermediates viz. $[\text{FeL}(\text{OH})(\text{CN})_x]^{2-n-x}$ and $[\text{NiL}(\text{CN})_x]^{2-n-x}$ where L = aminopolycarboxylate ligands and n being the charge on the same, formed in a multistep reaction of $[\text{NiL}]^{2-n-\text{CN}^{15,27}}$ and $[\text{FeL}(\text{OH})]^{2-n-\text{CN}^{28}}$ systems, have been determined by the use of ligand substitution rates. In multistep reaction this has not been possible by any other means because of their transient existence or extremely small concentration. A brief discussion on the same has been included in chapter-II.5.7.

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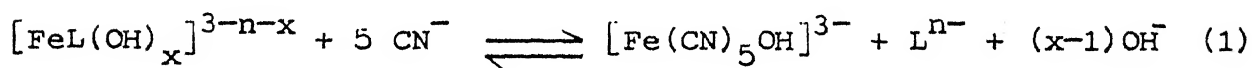
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CHAPTER II

KINETICS AND MECHANISM OF PENTACYANOHYDROXOFERRATE(III) FORMATION FROM MONOAMINOCARBOXYLATO FERRATE(III) COMPLEXES

ABSTRACT

The kinetics and mechanism of the reaction system:



where $\text{L}^{n-} = \text{HPDTA}^{4-}$ (2-hydroxy 1,3-diaminopropanetetraacetate anion) and HIDA^{2-} (N-(2-hydroxyethyl)iminodiacetate anion) have been investigated spectrophotometrically at 395 nm (λ_{max} of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$). The reaction conditions are: temp. = 25°C , pH = 10.5 ± 0.02 and $I = 0.25\text{M}$ (NaClO_4) for HPDTA, and pH = 9.5 ± 0.02 , $I = 0.1\text{M}$ (NaClO_4) for HIDA. The data show that the reactions have three distinguishable stages; the first stage is formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$, the second is conversion of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ and last is the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ by the respective ligands released during the first stage of

reaction. A variable order dependence in cyanide is observed ranging from one at high to three at low concentration of cyanide for $[\text{FeHPDTA}(\text{OH})]^{2-}$. In the reaction between $[\text{FeHIDA}(\text{OH})_2]^{1-}$ and cyanide ion, however, an interesting feature is that the order in cyanide concentration becomes zero at low cyanide concentration ($\leq 6 \times 10^{-3} \text{M}$) and one at high cyanide concentration. The formation of mixed ligand complexes of the type $[\text{FeL}(\text{OH})(\text{CN})_x]^{2-n-x}$ has been proposed for both the systems. The first stage of the reaction is kinetically controlled by the presence of four cyanide ions around the central iron atom in the rate-determining step. The reaction in the second stage is common to both the systems and follows a first order dependence on the concentration of $[\text{Fe}(\text{CN})_5\text{OH}]^3$ as well as cyanide, and overall second order. The third stage of reaction follows an overall second order kinetics, first order each in $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{L}^{n-}]$.

The thermodynamically unfavourable reverse reaction i.e. the reaction between $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and L^{n-} can be forced only in presence of large excess of L^{n-} over $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and exhibits first-order dependence each in $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and $[\text{L}^{n-}]$ and an inverse first-order dependence in cyanide. This makes it possible to identify the fourth step as the rate-determining one. The reaction rate is highly dependent on the hydroxyl ion concentration. The rate of reaction increases between pH 8.5-12. The ionic strength dependence of the forward rate constant is consistent

with the supposition that the fourth step is rate-determining in the proposed five step mechanism for the first stage of reaction. Activation parameters provide further support for the proposed mechanism.

A linear free-energy relationship has been proposed between stepwise rate constants and the overall stability constants of the intermediates viz. $[\text{FeL}(\text{OH})(\text{CN})_x]^{2-n-x}$ ($x = 0, 1, 2 \text{ \& } 3$) reacting in the particular steps.

II.2 Introduction

The formation of tetracyanonickelate(II) from the reaction of aminocarboxylatonickelate(II) with cyanide ions has been studied extensively.¹⁻¹¹ The polyaminocarboxylates of Co(II)¹² have also been investigated in respect of their exchange reactions with cyanide ions. Substitution kinetics of the reactions of Fe(II) complexes of some ligands viz., 1,10-phenanthroline,¹³⁻¹⁴ 2,2'-bipyridyl¹⁵ and Schiff's bases¹⁶ with cyanide ions have been reported. Recently, the reaction between pyridylazoresorcinol complexes of Fe(II) and Fe(III) with cyanide ions has been studied.¹⁷ More recently detailed kinetic studies have been carried out on some substitution reactions of aminocarboxylato ferrate(III) by cyanide ions.¹⁸⁻²² In order to obtain a better insight into the pathway of this reaction, we have chosen to investigate the reaction as represented by eqn. (1).

II.3 Experimental

Purified and recrystallized forms of HPDTA (Fluka), HIDA (Fluka, AG), NaClO_4 (E. Merck, F.R.G.), Ferric nitrate (May and Baker, U.K.) and $\text{Na}_3[\text{Fe}(\text{CN})_6]$ (GR, SDS) are used in this study. NaCN has been procured from May and Baker Ltd., England. Sodium aquopentacyanoferrate(II) prepared from sodium nitroprusside (AR, BDH) by a literature method,²³ is oxidised by H_2O_2 and then converted to aquopentacyanohydroxoferrate(III) by increasing the pH to a value higher than 10.²⁴ Ferric perchlorate has been prepared by dissolution of a precipitate of $\text{Fe}(\text{OH})_3$ in calculated amount of HClO_4 and standardized complexometrically using sulphosalicyclic acid as an indicator.²⁵ The perchlorate has been used for the preparation of $[\text{FeL}(\text{OH})]^{2-n}$ complexes (L = HPDTA and HIDA). A 20% excess of ligand over stoichiometric requirement is added to $\text{Fe}(\text{ClO}_4)_3$ solution for ensuring complete complexation. The NaCN is standardized argentometrically.²⁶ The pH of the reaction mixture is adjusted by addition of NaOH or HClO_4 . Buffers are not used in order to minimise complexity of the reaction system. The pH changes during the course of reaction have been found to be negligible within limits of experimental error. Through out the experimental work triple distilled water has been used for preparation of solutions and rinsing of glass ware.

A Toshniwal spectrophotometer model RL-02 (Beckman DU Type) equipped with a circulatory arrangement for thermostating the cell compartment has been used for all kinetic studies on these reactions. An ultracryostat model 2 NBE (VEB Kombinat Medizin and Labortechnik Kombinatbetrieb, GDR) has been used for maintenance of the desired temperature. A Shimadzu model UV-240 double beam spectrophotometer has been used for repetitive scans of the reaction mixture. pH measurements are recorded on an Elico digital pH meter model LI-120 using BDH buffers for standardization.

II.4 Kinetic Measurements

The rate of formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ is followed at 395 nm (λ_{max} of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$, $\epsilon = 1740 \text{ M}^{-1}\text{cm}^{-1}$)²⁷ at pH = 10.5 ± 0.02 , $I = 0.25\text{M}$ (NaClO_4) and 25°C for $L = \text{HPDTA}$ and pH = 9.5 ± 0.02 , $I = 0.1\text{M}$ (NaClO_4) and 25°C for $L = \text{HIDA}$ in the presence of large excess of cyanide. The names and structures of chosen aminocarboxylates are given in Table II.1. The spectra of $[\text{FeL}(\text{OH})]^{2-n}$ and $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ are given in Fig. II.1 and Fig. II.2 respectively. Pseudo-first-order plots of $\log C_A$ versus time are obtained over at least 70 % of the reaction in all the cases. C_A is the concentration of $[\text{FeL}(\text{OH})]^{2-n}$ or $[\text{FeL}(\text{OH})_2]^{1-n}$ at any time t and n is the charge on the ligand under consideration. At the chosen wavelength, $[\text{FeL}(\text{OH})_x]^{3-n-x}$ complexes absorb to some extent.

Table II.1. Names and structures of the aminopolycarboxylate anions.

L^{n-}	Name	Structure
HPDTA ⁴⁻	2-Hydroxy-1,3-diaminopropane N,N,N',N'-tetraacetate anion	$ \begin{array}{c} ^-OCH_2C \\ \diagup \\ N \cdot CH_2 \cdot \underset{\substack{ \\ OH}}{CH} \cdot CH_2 \cdot N \begin{array}{l} \diagup CH_2COO^- \\ \diagdown CH_2COO^- \end{array} \\ \diagdown \\ ^-OCH_2C \end{array} $
HIDA ²⁻	N-(2-Hydroxyethyl)-iminodiacetate anion	$ HOCH_2 \cdot CH_2 \cdot N \begin{array}{l} \diagup CH_2COO^- \\ \diagdown CH_2COO^- \end{array} $

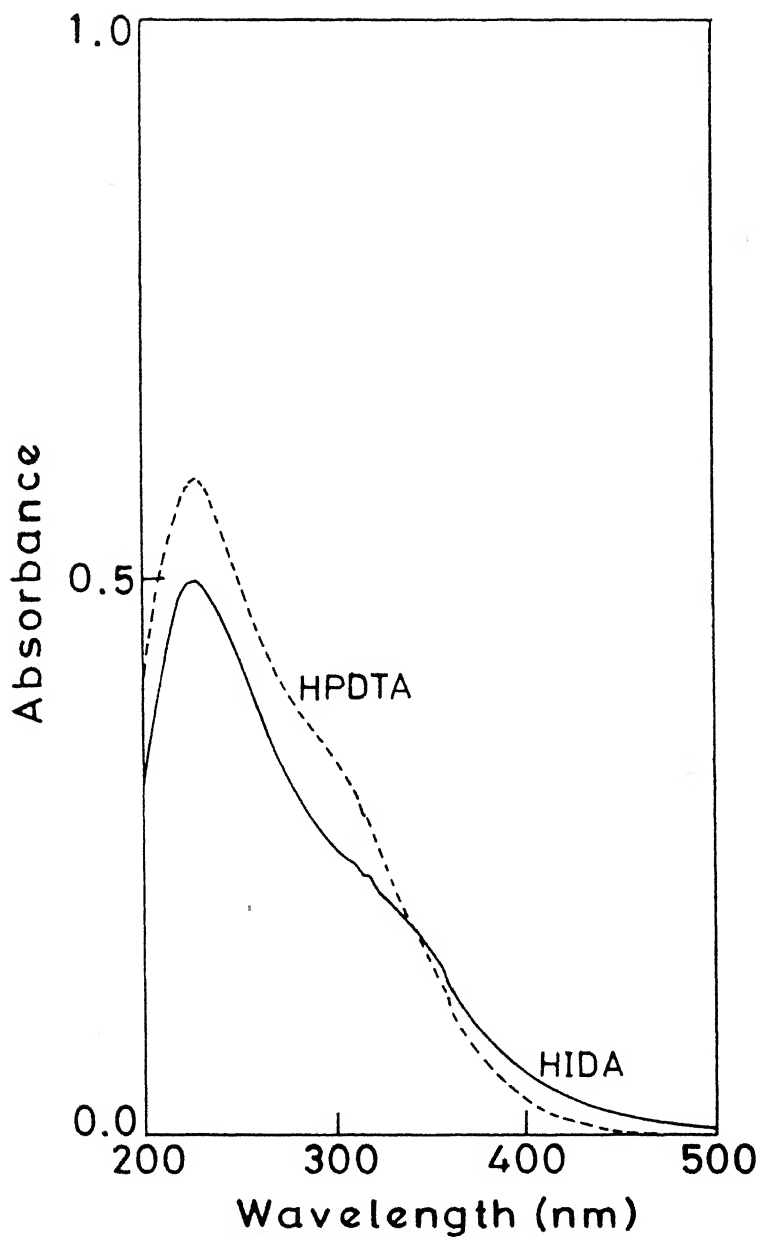


Fig. II.1 Absorption spectra of $[\text{FeL}(\text{OH})_x]^{3-n-x}$ complexes. $[\text{FeL}(\text{OH})_x^{3-n-x}] = 10^{-4} \text{ M}$, pH = 11.0 and 9.5 for L = HPDTA and HIDA respectively.

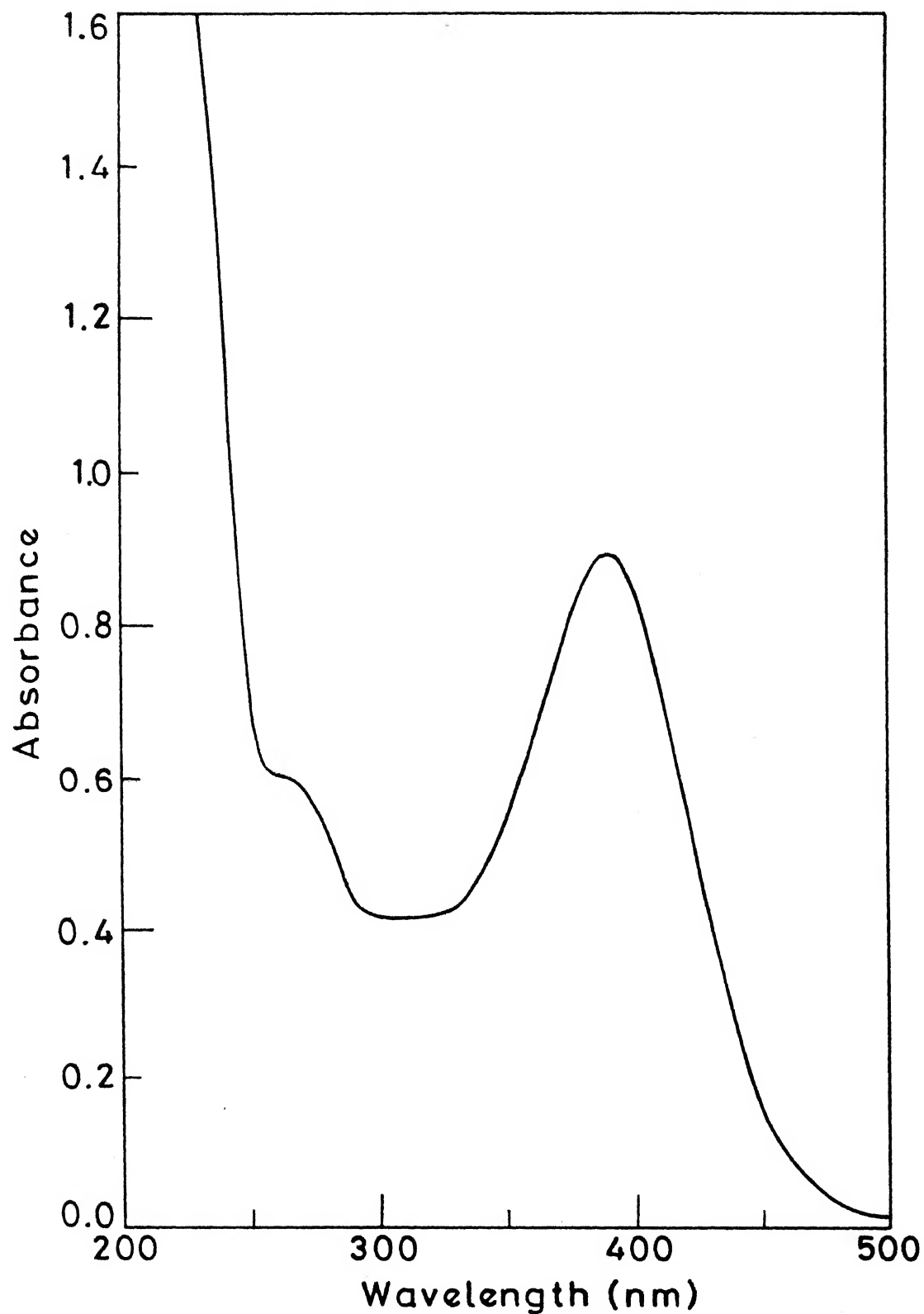


Fig.II.2 Absorption spectrum of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$;
 $[\text{Fe}(\text{CN})_5\text{OH}]^{3-} = 5 \times 10^{-4} \text{ M}$ at $\text{pH} = 11.0 \pm 0.02$.

So a correction is applied for the absorption of $[\text{FeL}(\text{OH})]^{2-n}$ and $[\text{FeL}(\text{OH})_2]^{1-n}$ at 395 nm. Based on reaction (1), an expression used for the calculation of C_A , is formulated as

$$C_A = (\epsilon_B C_A^0 - A_t) / (\epsilon_B - \epsilon_A) \quad (2)$$

where $A = [\text{FeL}(\text{OH})_x]^{3-n-x}$, $B = [\text{Fe}(\text{CN})_5\text{OH}]^{3-}$, ϵ_A and ϵ_B are the respective ϵ 's of A and B, C_A^0 is the initial concentration of $[\text{FeL}(\text{OH})_x]^{3-n-x}$ ($x = 1$ for HPDTA and 2 for HIDA).

The reverse reactions have also been followed at 395 nm (λ_{max} of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$) by disappearance of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ with time in presence of ligands, L^{n-} , taken in large excess. The reaction between $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and cyanide ions has already been investigated in our laboratory and the results are discussed at appropriate place.

II.5 Results

II.5.1 Species distribution of metal complexes and polyaminocarboxylates as a function of pH

The metal ligand complexes as well as the ligands coordinated to the metal centre can exist in several protonated and unprotonated forms. It is necessary, therefore, to know the kind of reactant species and their relative concentrations at a specified set of experimental conditions viz. pH, temperature, ionic

strength and concentration during a kinetic investigation . The species distribution of various protonated and unprotonated forms of ligand and metal complexes is calculated from a computer programme originally given by Perrin and Sayce,²⁸ using a Dec-10 system.

Here a brief discussion for the same follows: At any given pH the concentration, in percent, of a particular form of a ligand (aminopolycarboxylates in the present case) can be obtained by means of equation (3).

$$a_{\text{LH}}^{(n-m)+} = \frac{[\text{H}^+]^{n-m} K_1 K_2 \dots K_m \times 100\%}{[\text{H}^+]^n + [\text{H}^+]^{n-1} K_1 + \dots + K_1 K_2 K_3 \dots K_m} \quad (3)$$

where n = No. of dissociable protons and m ($= 1, 2, 3 \dots$) is the number of species present. The values of pK_a 's of ligands and stability constants of metal complexes used in these calculations are given in Table II.2. The species distribution for the metal complexes can be calculated by an iterative method, starting with a crude approximation $[\text{M}^i] = [\text{M}^i]_T$ based on equation (4).

$$[\text{M}^i] = [\text{M}^i]_T + \sum_{j=1}^n P_{ij} C_j \quad (4)$$

where P_{ij} is the total number of ions of M^i in the j^{th} species. The species distribution for HPDTA and FeHPDTA, HIDA and FeHIDA are given in Fig. II.3 and Fig. II.4 respectively. The curves

Table II.2. A: Protonation constants of aminocarboxylates at 25°C (log K) and I = 0.1M (NaClO₄/KNO₃).

L^{n-}	HL	H_2L	H_3L	H_4L	Ref.
HPDTA ⁴⁻	9.49 ± 0.01	6.96 ± 0.01	2.6 ± 0.01	1.6	31
HIDA ²⁻	8.66 ± 0.02	2.2 ± 0.05	-	-	32-37

B: Stability constants of aminocarboxylato ferrate(III) complexes (log K) at 25°C and I = 0.1M(NaClO₄/KNO₃)

L^{n-}	FeL	FeL(OH)	FeL(OH) ₂	Ref.
HPDTA ⁴⁻	17.2	9.45	4.7	38
HIDA ²⁻	11.61	2.46	5.7	39

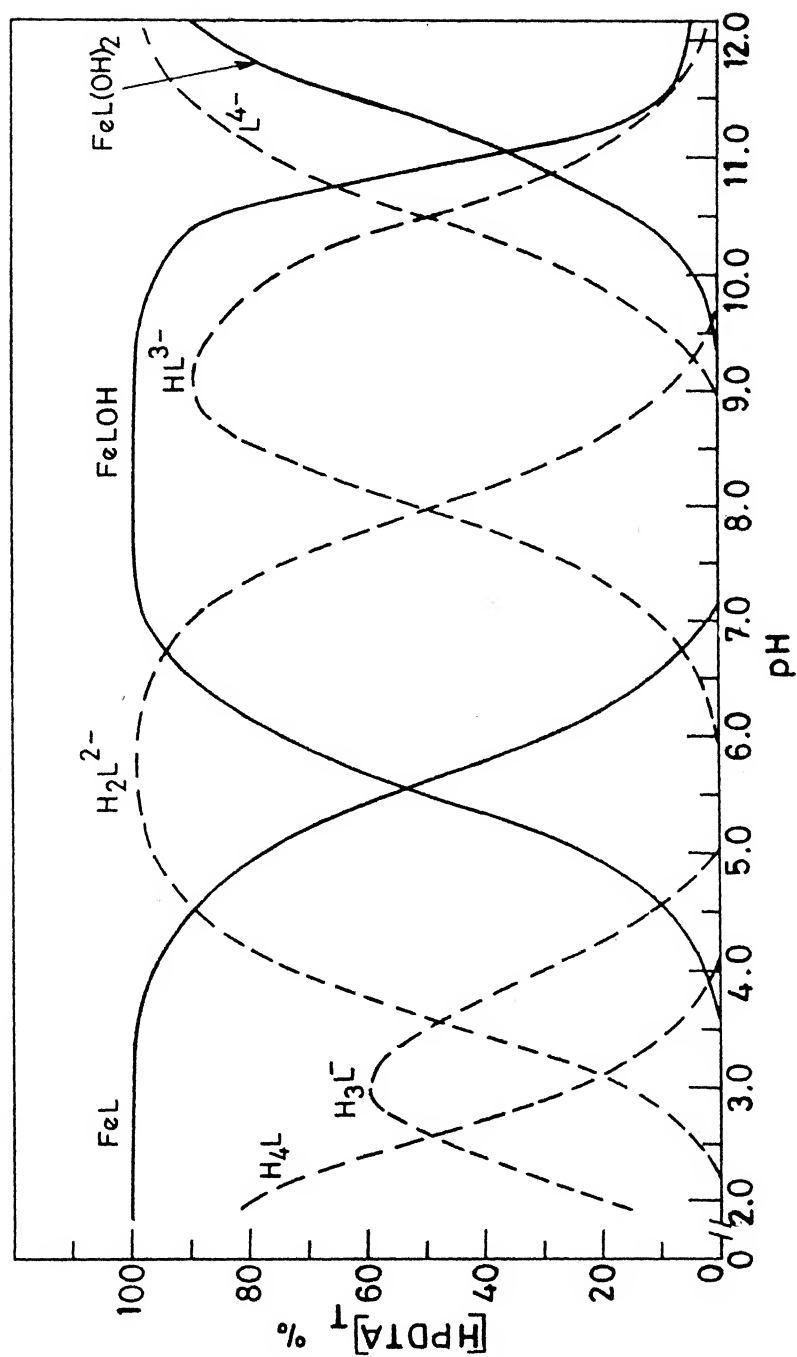


Fig. II.3 Species distribution of HPDTA and FeHPDTA as a function of pH; $[Fe^{3+}] = [HPDTA] = 2.5 \times 10^{-4} \text{ M}$.

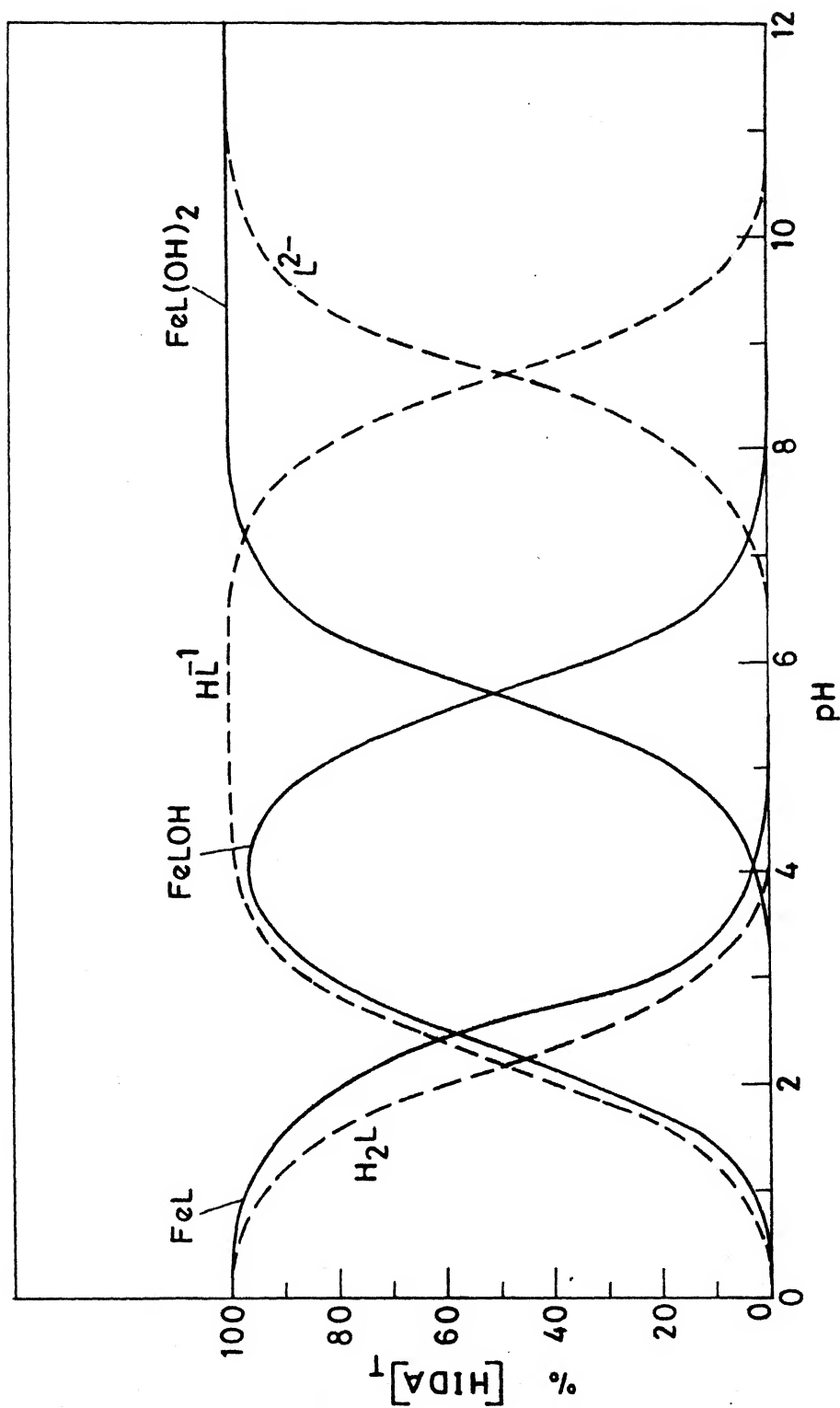


Fig.11.4 Species distribution of HIDA and FeHIDA as a function of pH ; $[HIDA] = [Fe^{3+}] = 2.5 \times 10^{-4} M$.

show that the $[\text{FeHPDTA}(\text{OH})]^{2-}$ and $[\text{FeHIDA}(\text{OH})_2]^{1-}$ are the principal reacting species in their exchange reactions with cyanide under the specified chosen conditions i.e. in the pH range of interest, ionic strength and temperature.

II.5.2 Kinetics of Forward reaction

The forward reaction is favoured thermodynamically ($K_{\text{FeHPDTA}(\text{OH})} = 10^{9.45}$, $K_{\text{FeHIDA}(\text{OH})_2} = 10^{9.15}$ and β_5 of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-} = 10^{43.6}$) as there is a large difference between the stability constants of the reactants and the products. During kinetic runs a significant observation is made that a small but instantaneous increase in the absorbances takes place immediately following mixing which is followed by relatively slow absorbance changes due to formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$. This suggests that mixed ligand complex(es) are produced immediately after mixing followed by slower formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$. Similar observations have also been made for the NiL-CN^{1-11} reaction systems by Margerum et al.,² Stara and Kopanica⁶ and Nigam et al. earlier.⁷⁻¹¹

The forward reactions for $[\text{FeHPDTA}(\text{OH})]^{2-}$ and $[\text{FeHIDA}(\text{OH})_2]^{1-}$ with cyanide under pseudo-first-order conditions are found to be first order in these complexes. In $[\text{FeHPDTA}(\text{OH})]^{2-}$ system, a variable order dependence in cyanide concentration changing from three to one is observed as the cyanide concentration changes from

low to high. But in the $[\text{FeHIDA}(\text{OH})_2]^{1-}$ system, a zero-order dependence in cyanide below concentration $\sim 6 \times 10^{-3}\text{M}$ and one at higher cyanide concentration have been observed. Similar observations have been made earlier²¹ in case of $[\text{FeTTHA}(\text{OH})_2]^{5-}$ CN^- system, where a zero-order dependence in cyanide below concentration $\sim 2.7 \times 10^{-4}\text{M}$ and a third order at higher cyanide concentration were seen. The significance of variable order and zero-order dependences in cyanide will be discussed later. The pseudo-first-order rate constants at different cyanide concentration levels (always taken in excess) are compiled in Table II.3. Plots of $\log k_{\text{obs}}$ versus $\log [\text{CN}^-]_{\text{T}}$ are given in Fig. II.5. $[\text{CN}^-]_{\text{T}}$ includes a small amount of HCN present at any chosen pH. In case of $[\text{FeHPDTA}(\text{OH})]^{2-}$ reaction system the slope of above plots are found to change from three to one as the cyanide concentration increases. On the other hand, a slope of one and zero at high and low concentration of cyanide respectively is observed in $[\text{FeHIDA}(\text{OH})_2]^{1-}$ reaction system. In both cases, an inverse-first-order dependence in cyanide concentration is observed in the kinetic study of reverse reactions.

The variable order dependence in cyanide ion concentration can be interpreted to infer that the formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ takes place in steps through the successive formation of mixed ligand intermediates $[\text{FeL}(\text{OH})(\text{CN})_x]^{2-n-x}$, and the observed order in cyanide depends upon the number of cyanide ions which are

Table II.3. Kinetics of formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ from $[\text{FeL}(\text{OH})_x]^{3-n-x}$ complexes in presence of excess cyanide at 25°C .

- A. $[\text{FeHPDTA}(\text{OH})^{2-}] = (1.0-2.5) \times 10^{-4} \text{ M}$, $\text{pH} = 10.5 \pm 0.02$ and $\text{I} = 0.25 \text{ M}(\text{NaClO}_4)$.
- B. $[\text{FeHIDA}(\text{OH})_2^{1-}] = (4.5-5.1) \times 10^{-4}$, $\text{pH} = 9.5 \pm 0.02$ and $\text{I} = 0.1 \text{ M}(\text{NaClO}_4)$.

A. $[\text{CN}^-]_{\text{T}}, 10^2, \text{M}$	$k_{\text{obs}}, \text{s}^{-1}$	$k_{\text{f}} (= k_{\text{obs}} / [\text{CN}^-]^x), \text{M}^{-1} \text{s}^{-1}$
2.0	1.42×10^{-5}	1.78
3.0	3.80×10^{-5}	1.43
4.0	1.18×10^{-4}	1.84
5.0	2.65×10^{-4}	2.12
<hr/>		
$k_{\text{f}}(\text{av}) = (1.79 \pm 0.25), \text{M}^{-3} \text{s}^{-1}$		
5.0	2.65×10^{-4}	1.06×10^{-1}
6.0	5.22×10^{-4}	1.45×10^{-1}
8.0	7.13×10^{-4}	1.11×10^{-1}
<hr/>		
$k_{\text{f}}(\text{av}) = (1.21 \pm 0.17) \times 10^{-1}, \text{M}^{-2} \text{s}^{-1}$		
9.0	9.21×10^{-4}	1.02×10^{-2}
10.0	1.21×10^{-3}	1.21×10^{-2}
15.0	1.6×10^{-3}	1.07×10^{-2}
20.0	2.05×10^{-3}	1.03×10^{-2}
25.0	2.55×10^{-3}	1.02×10^{-2}
<hr/>		
$k_{\text{f}}(\text{av}) = (1.07 \pm 0.07) \times 10^{-2}, \text{M}^{-1} \text{s}^{-1}$		

...contd.

Table II.3(contd.)

B. $[\text{CN}^-]_{\text{T}}, 10^2, \text{M}$	$k_{\text{obs}}, 10^4, \text{s}^{-1}$	$k_{\text{f}} (= k_{\text{obs}} / [\text{CN}^-]^x), \text{s}^{-1} \text{ or } \text{M}^{-1} \text{s}^{-1}$
0.45	2.14	2.14×10^{-3}
0.50	2.15	2.15×10^{-3}
0.60	2.14	2.14×10^{-3}
<hr/>		
		$k_{\text{f}}(\text{av}) = (2.14 \pm .004) \times 10^{-3}, \text{s}^{-1}$
1.0	2.45	2.45×10^{-2}
2.0	4.28	2.14×10^{-2}
2.5	5.41	2.16×10^{-2}
3.0	5.75	1.92×10^{-2}
4.0	8.52	2.13×10^{-2}
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		$k_{\text{f}}(\text{av}) = (2.16 \pm 0.17) \times 10^{-2}, \text{M}^{-1} \text{s}^{-1}$

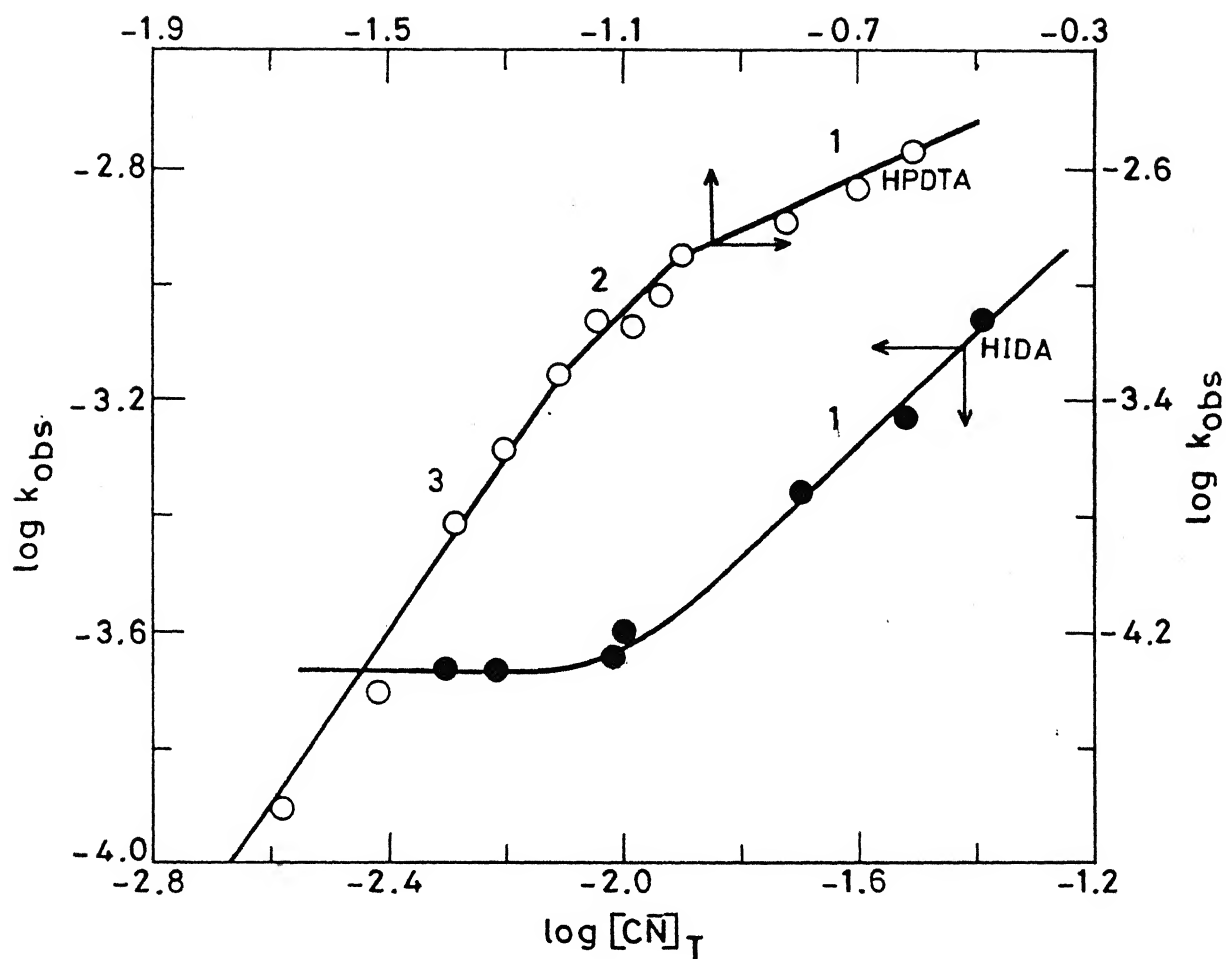


Fig.II.5 The cyanide dependence of observed pseudo-first-order rate constants for $[\text{FeL}(\text{OH})_x]^{3-n-x} \cdot \text{CN}^-$. (The conditions as given in Table II.3.)

already complexed to the FeL(OH) complex in any particular step. A general rate expression consistent with a variable order dependence in cyanide is given in equation (5).

$$\begin{aligned} \text{Rate} &= \frac{d[\text{Fe(CN)}_5\text{OH}^{3-}]}{dt} = k_{\text{obs}} [\text{FeL(OH)(CN)}_x]^{2-n-x} \\ &= k_f [\text{FeL(OH)(CN)}_x]^{2-n-x} [\text{CN}^-]^{4-x} \quad (5) \end{aligned}$$

where n is the charge on the ligand L and x is the number of cyanides attached to $[\text{FeL(OH)(CN)}_x]^{2-n-x}$ complexes and can have values one, two and three for HPDTA system while zero and one for HIDA system. The kinetics of reverse reaction helps in identifying the rate-determining step as the fourth one in a five step mechanism (vide supra).

II.5.2.1 pH dependence

The pH ($= -\log[\text{H}^+]$ for dilute solutions) profiles for both reactions have been investigated. The pH ranges are 9.5-11.0 and 8.5-10.5 for $[\text{FeHPDTA(OH)}]^{2-}$ and $[\text{FeHIDA(OH)}_2]^{1-}$ systems respectively. The values of observed forward rate constants are given in Table II.4. The rates of forward reaction for both systems are found to increase in their respective pH ranges mentioned above and finally level off. These measurements are made in conditions where the order dependence in cyanide concentration is one. The

Table II.4. Effect of pH on formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ at 25°C .

A. $[\text{FeHPDTA}(\text{OH})^{2-}] = 2.5 \times 10^{-4}\text{M}$, $[\text{CN}^-]_{\text{T}} = 1.5 \times 10^{-1}\text{M}$
and $\text{I} = 0.25\text{M}(\text{NaClO}_4)$.

B. $[\text{FeHIDA}(\text{OH})_2^{1-}] = 5.0 \times 10^{-4}$, $[\text{CN}^-]_{\text{T}} = 2.5 \times 10^{-2}\text{M}$
and $\text{I} = 0.1\text{M}(\text{NaClO}_4)$.

A.	pH	$k_{\text{obs}}, \text{s}^{-1}$	$k_{\text{f}} (=k_{\text{obs}}/[\text{CN}^-]), \text{M}^{-1}\text{s}^{-1}$
	9.5	1.50×10^{-5}	1.0×10^{-4}
	9.72	2.79×10^{-5}	1.77×10^{-4}
	10.0	1.60×10^{-3}	1.07×10^{-2}
	10.5	1.63×10^{-3}	1.09×10^{-2}
	10.73	1.83×10^{-3}	1.22×10^{-2}
	11.0	1.97×10^{-3}	1.24×10^{-2}

B.	pH	$k_{\text{obs}}, 10^4, \text{s}^{-1}$	$k_{\text{f}}, 10^2, \text{M}^{-1}\text{s}^{-1}$
	8.5	3.69	1.50
	9.0	4.30	1.70
	9.25	5.11	2.0
	9.5	5.41	2.16
	10.0	5.41	2.16
	10.5	5.40	2.16

initial steep portion of the curves shown in Fig. II.6, reflects the changes in rate as $\text{FeHPDTA}(\text{H}_2\text{O})$ and $\text{FeHIDA}(\text{H}_2\text{O})_2$ are converted to the more reactive $\text{FeHPDTA}(\text{OH})$ and $\text{FeHIDA}(\text{OH})_2$ species respectively on raising the pH. The limiting values of the rate constants are due to the reactions of the two hydroxo complexes viz. $\text{FeHPDTA}(\text{OH})$ and $\text{FeHIDA}(\text{OH})_2$ (which are the predominant reacting species present above $\text{pH} = 9.5$) and cyanide ions. In some earlier investigations on ligand exchange reactions, it has been possible to resolve the rates due to various reactive species by algebraic manipulation.¹¹ It has not been possible to do so in the present systems (viz. $\text{FeL}(\text{OH})_x\text{-CN}^-$; $\text{L} = \text{aminocarboxylates}$) because of the complexity arising due to subsequent reactions involving the conversion of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ and eventual reduction of the latter to $[\text{Fe}(\text{CN})_6]^{4-}$.

II.5.2.2 Ionic Strength dependence

The forward reaction rates are found to increase with increase in ionic strength of the medium. The ionic strength is maintained each time before mixing the two reactants keeping pH, temperature and initial concentrations constant during these kinetic runs. The forward second order rate constants for the reaction of $[\text{FeHPDTA}(\text{OH})]^{2-}$ and $[\text{FeHIDA}(\text{OH})_2]^{1-}$ with cyanide ion follow Bronsted-Bjerrum equation.(6).

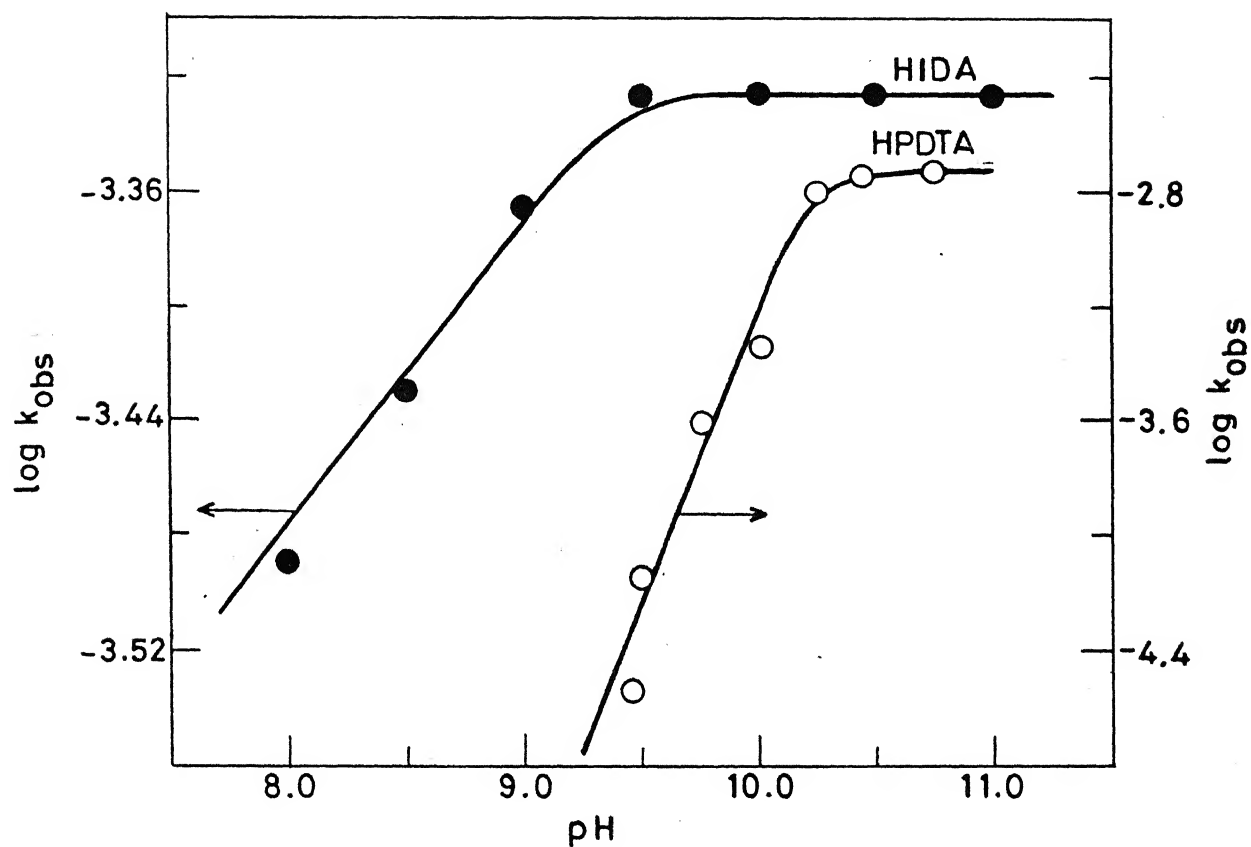


Fig.II.6 Effect of pH on the forward reaction of cyanide with $[\text{FeL}(\text{OH})_x]^{3-n-x}$ complexes. The conditions are given in Table II.4 .

$$\log k_f = \log k_o + 1.02 Z_A Z_B \sqrt{I} \quad (6)$$

where k_f is the specific rate constant, k_o is the specific rate constant at zero ionic strength, and Z_A, Z_B are the charges on the two reactant species. The plots of $\log k_f$ versus \sqrt{I} for both the systems are given in Fig. II.7. The values of k_{obs} and k_f at different ionic strength are listed in Table II.5. The values of $Z_A Z_B$ calculated from the slopes of these plots agree closely with the expected values envisaged in the rate-determining step.

II.5.3 Kinetics of Reverse reaction

The reverse reaction of equation (1) is not favoured thermodynamically and it becomes possible to force the same only by adding a relatively large excess of ligands compared to $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$. At pH = 10.5-11.0, $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ shows no noticeable dissociation even after prolonged standing. The rate of decomposition of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ in presence of L^{n-} is first order each with respect to concentration of the respective ligands and $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ but exhibits an inverse-first-order dependence with respect to $[\text{CN}^-]$. The disappearance of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ follows the rate expression given in equation (7).

$$-d[\text{Fe}(\text{CN})_5\text{OH}^{3-}]/dt = k_r[\text{Fe}(\text{CN})_5\text{OH}^{3-}][\text{L}^{n-}]/[\text{CN}^-] \quad (7)$$

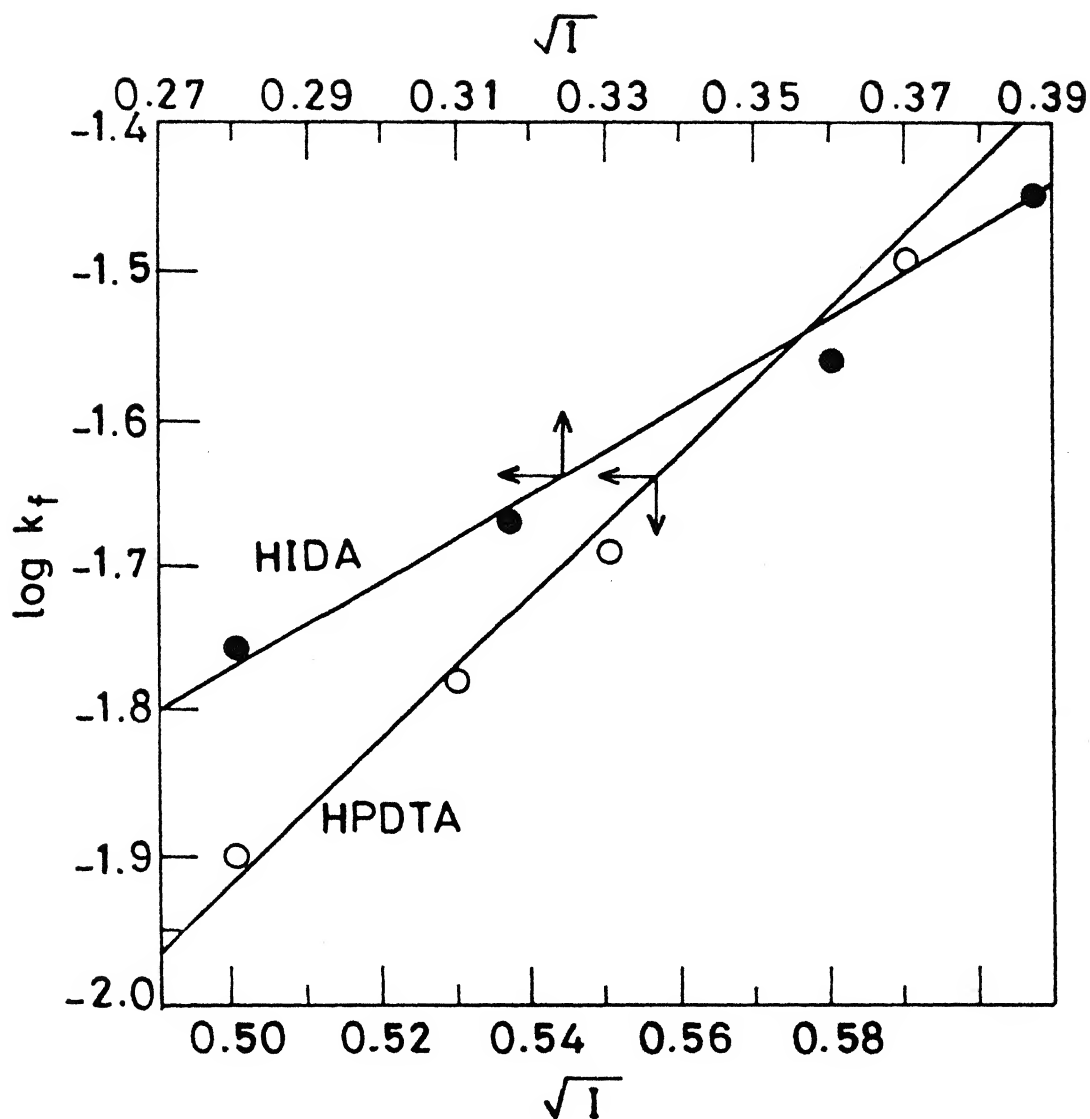


Fig.II.7 Ionic strength dependence of observed pseudo-first-order rate constants for $[\text{FeL}(\text{OH})_x]^{3-n-x} - \text{CN}^-$ reactions. The conditions as given in Table II.5.

Table II.5. Effect of ionic strength on the forward reaction rate for the reaction of cyanide ion with $[\text{FeL}(\text{OH})_x]^{2-n-x}$ complexes at 25°C.

A. $[\text{FeHPDTA}(\text{OH})^{2-}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{CN}^-] = 1.5 \times 10^{-1} \text{ M}$,
and $\text{pH} = 10.5 \pm 0.02$

B. $[\text{FeHIDA}(\text{OH})_2^{1-}] = 4.0 \times 10^{-4} \text{ M}$, $[\text{CN}^-] = 2.5 \times 10^{-2} \text{ M}$
and $\text{pH} = 9.5 \pm 0.02$

A.	I, M(NaClO_4)	$k_{\text{obs}}, 10^3, \text{s}^{-1}$	$k_{\text{f}}, 10^2, \text{M}^{-1} \text{s}^{-1}$
	0.25	2.47	1.65
	0.29	3.41	2.27
	0.35	4.82	3.21

B.	I, M(NaClO_4)	$k_{\text{obs}}, 10^4, \text{s}^{-1}$	$k_{\text{f}}, 10^2, \text{M}^{-1} \text{s}^{-1}$
	0.08	4.33	1.73
	0.10	5.41	2.16
	0.13	6.88	2.75
	0.15	8.63	3.45

The integrated form of equation (7) in presence of large excess of L^{n-} is written as

$$(A_i - A_t) + A_i \ln A_t/A_i = -\epsilon \cdot l \cdot k'_{obs} \cdot t/5 \quad (8)$$

where A_i and A_t are absorbances at time $t = 0$ and $t = t$ respectively, l is the path length and ϵ is the molar extinction coefficient of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ at the wavelength at which the reaction is monitored. The plots of $([A_i - A_t] + A_i \ln A_t/A_i)$ versus time give straight lines and slopes of these plots give k'_{obs} , where $k'_{obs} = k_r[L^{n-}]$, k_r being the reverse rate constants. Inverse first-order plots for reaction of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ with HIDA are shown in Fig.II.8. The plots for HPDTA systems are similar and are, therefore, not shown. The rate constants obtained from these plots are given in Table II.6. The reverse rate study has made it possible to pin point the rate-determining step as the penultimate one in a stepwise mechanism proposed by us ²¹ (vide supra).

II.5.4 Temperature dependence of Forward and Reverse rates

The temperature dependence of the forward rates is found to follow the Arrhenius equation over the temperature range 25-45°C and 15-31°C for $\text{FeHPDTA}(\text{OH})-\text{CN}^-$ and $\text{FeHIDA}(\text{OH})_2-\text{CN}^-$ reaction systems respectively. The reverse rate also obeys the Arrhenius equation (9) over the temperature range 25-45°C.

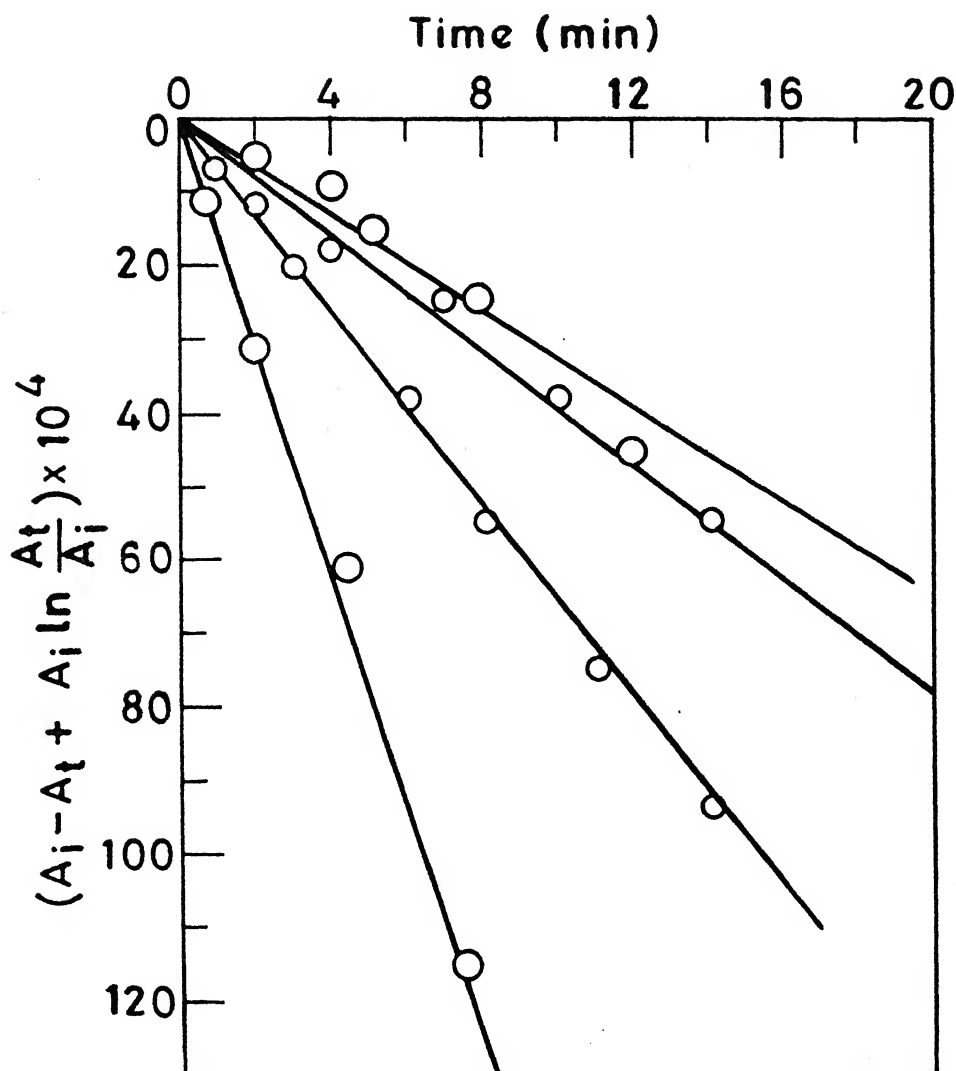


Fig.II. 8 Inverse-first-order plots for reaction of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ with HIDA at temp.=35°C, pH = 11.0, $I = 0.1\text{M}$ (NaClO_4)

Table II.6. Rate constants for the reverse reaction.

A. $L^{n-} = \text{HPDTA}^{4-}$; $\text{pH} = 10.5 \pm 0.02$; $I = 0.92\text{M}(\text{NaClO}_4)$,
 $[\text{Fe}(\text{CN})_5\text{OH}^{3-}] = (0.7 - 1.0) \times 10^{-4}\text{M}$ and $\text{temp.} = 25 \pm 0.1^\circ\text{C}$.

$[\text{HPDTA}^{4-}]_T, \text{M}$	$10^9, k'_{\text{obs}} \text{ms}^{-1}$	$10^8, k_r (=K_5^{-1}k_{-4}), \text{s}^{-1}$
0.05	2.99	5.98
0.10	6.45	6.40
0.12	7.18	5.98

$$k_r(\text{av}) = (6.1 \pm 0.2) \times 10^{-8}, \text{s}^{-1}$$

B. $L^{n-} = \text{HIDA}^{2-}$; $\text{pH} = 11 \pm 0.01$ and $I = 0.1\text{M}(\text{NaClO}_4)$,
 $[\text{Fe}(\text{CN})_5\text{OH}^{3-}] = 5 \times 10^{-5}\text{M}$, and $\text{temp.} = 35 \pm 0.1^\circ\text{C}$.

$[\text{HIDA}^{2-}]_T, \text{M}$	$10^9, k'_{\text{obs}} \text{ms}^{-1}$	$10^8, k_r (=K_5^{-1}k_{-4}), \text{s}^{-1}$
0.1	1.68	1.68
0.15	2.39	1.59
0.21	3.83	1.82

$$k_r(\text{av}) = (1.7 \pm 0.1) \times 10^{-8}, \text{s}^{-1}$$

$$\ln k = -E_a/RT + \ln A \quad (9)$$

The values of entropy of activation ΔS^\ddagger for the forward and reverse reactions are calculated from the Eyring equation (10)

$$k_2 = \frac{k_B \cdot T}{h} \cdot e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S^\ddagger/R} \quad (10)$$

where all terms have their usual meanings. The above equation (10) can also be written as equation (11).

$$k_2 = P_z \cdot e^{\Delta H^\ddagger/RT} \quad (11)$$

where P_z is the probability factor defined in the expression

$$P_z = \frac{k_B \cdot T}{h} \cdot e^{\Delta S^\ddagger/R} \quad (12)$$

The values of activation parameters (ΔH^\ddagger and ΔS^\ddagger) for forward reactions have been determined in conditions where the order in cyanide concentration is one and, therefore, for the rate-determining step itself. The activation parameters are also calculated for the reaction between $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and cyanide ion which has been studied earlier in our laboratory and is common for both the systems. The values of these parameters are listed in Table II.7 for the sake of completeness.

Table II.7. Activation parameters for forward^{a,b} and reverse^c reaction.

Reaction	L^{n-}	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹
a) $[\text{FeL}(\text{OH})_x]^{3-n-x} + 5\text{CN}^-$	HPDTA ⁴⁻	31.2 ± 2.0	-178 ± 3
— $[\text{Fe}(\text{CN})_5\text{OH}]^{3-} + L^{n-} + (x-1)\text{OH}^-$	HIDA ²⁻	5.9 ± 1.0	-258 ± 2
b) $[\text{Fe}(\text{CN})_5\text{OH}]^{3-} + \text{CN}^-$		36.5	-168 ± 3
— $\longrightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{OH}^-$			
c) $[\text{Fe}(\text{CN})_5\text{OH}]^{3-} + L^{n-}$	HPDTA ⁴⁻	64.1 ± 2.2	-176 ± 3
— $\longrightarrow [\text{FeL}(\text{OH})]^{2-n} + \text{CN}^-$	HIDA ²⁻	44.6 ± 2.0	-232 ± 2

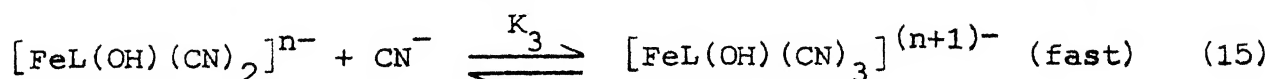
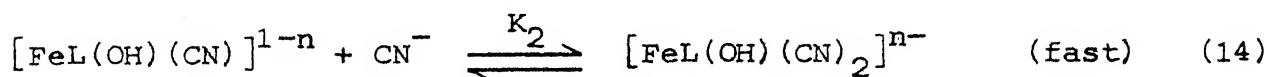
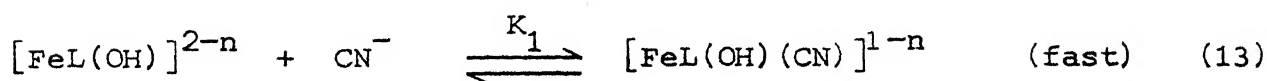
^b Ref. 47.

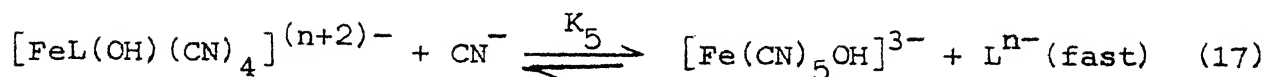
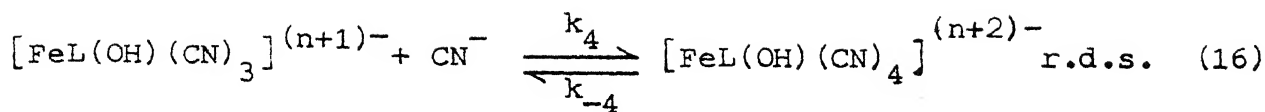
II.5.5 Reaction between $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ and L^{n-}

As the concentration of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ produced in the first stage of reactions increases, it begins to react with cyanide present in excess to form $[\text{Fe}(\text{CN})_6]^{3-}$ which in turn reacts with the ligand, released in the first stage of reaction to form $[\text{Fe}(\text{CN})_6]^{4-}$ and the oxidation products of the respective ligands. Similar reactions have been shown to occur with other ligand systems viz. ethylenediaminetetraacetate anion (EDTA^{4-}),⁴⁰ diethylenetriaminepentaacetate anion (DTPA^{5-}).⁴¹ The products of these reactions, according to earlier studies,⁴⁰ are $[\text{Fe}(\text{CN})_6]^{4-}$ and polybasic aliphatic acids e.g. glycollic acid, simpler amino-polycarboxylates, carbondioxide and ammonia.

II.5.6 Discussion

Based on the experimental observations on the forward and reverse rates of the reaction between $[\text{FeL}(\text{OH})]^{2-n}$ ($\text{L}^{n-} = \text{HPDTA}^{4-}$ and HIDA^{2-}) and cyanide ions, a general five step mechanism is proposed as given from equation (13) to equation (17).





The HPDTA reaction exhibits a variable order in cyanide which ranges from one to three while in case of HIDA, the order varies from zero to one. The implication of zero order dependence will be treated later.

A general expression which accounts for all the observed orders in cyanide concentration is formulated in equation (18).

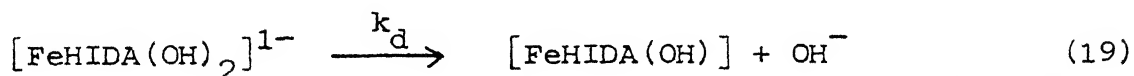
$$k_{\text{obs}} = \frac{K_1 K_2 K_3 k_4 [\text{CN}^-]^4}{1 + K_1 [\text{CN}^-] + K_1 K_2 [\text{CN}^-]^2 + K_1 K_2 K_3 [\text{CN}^-]^3} \quad (18)$$

Fourth, third, second and first order dependences in [cyanide] can be deduced from the above expression at various levels of cyanide concentrations. Thus a fourth order dependence is expected at very low cyanide concentration when the last three terms in the denominator are very much smaller than unity.

In case of HPDTA systems it is proposed that the first step is very fast and a stable 1:1:1 intermediate $[\text{FeL}(\text{OH})(\text{CN})]^{1-n}$ is formed instantaneously even at very low cyanide concentration. Once this is achieved the variable order changing from three to one becomes understandable from the occurrence of three remaining

steps upto the rate-determining step. At very small concentration of cyanide where the fourth order dependence might have been observed the rate becomes too slow for dependable measurements. The fourth order rate constant can, however, be obtained by an algebraic manipulation, discussed later.

In case of HIDA reaction, however, the order in cyanide at moderate and high $[\text{CN}^-]$ is found to be one. This indicates the rapid formation of the stable 1:1:3 intermediate $[\text{FeL}(\text{OH})(\text{CN})_3]$ which reacts with one cyanide in the rate-determining step giving rise to only the observed first order dependence at medium and high cyanide concentration. Besides this, the HIDA system shows an additional interesting behaviour. It also exhibits a zero-order dependence at low cyanide concentration. A zero-order dependence in cyanide has also been observed in the reaction between $[\text{FeTTHA}(\text{OH})_2]^{5-}$ and cyanide ions studied earlier.²¹ This indicates that in the first stage of reaction the dihydroxy species undergoes a very slow dissociation according to equation (19).



Subsequent to this dissociation the remaining steps in the reaction of $[\text{FeHIDA}(\text{OH})]$ with cyanide ions follow the same mechanistic scheme as presented from equation (13) to equation (17).

The rate expression for the reverse reaction can be derived in terms of the concentration of the intermediate in the rate-determining step. Thus

$$\text{Reverse Rate} = k_{-4} [\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} \quad (20)$$

The concentration of the intermediate can be obtained by application of steady state treatment to this species.

$$\begin{aligned} d[\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} / dt &= k_4 [\text{FeL}(\text{OH})(\text{CN})_3]^{(n+1)-} [\text{CN}^-] \\ &- k_{-4} [\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} - k_5 [\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} [\text{CN}^-] \\ &+ k_{-5} [\text{Fe}(\text{CN})_5\text{OH}^{3-}] [\text{L}^{n-}] = 0 \end{aligned} \quad (21)$$

$$[\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} = \frac{k_4 [\text{FeL}(\text{OH})(\text{CN})_3]^{(n+1)-} [\text{CN}^-] + k_{-5} [\text{Fe}(\text{CN})_5\text{OH}^{3-}] [\text{L}^{n-}]}{k_{-4} + k_5 [\text{CN}^-]} \quad (22)$$

The first term of the numerator can be ignored in presence of excess of ligand. A combination of forward and reverse rate study has shown that the fifth step is a fast one compared to the fourth one and values of k_4 and also k_{-4} must be relatively small compared to k_5 ($k_{-4} < k_5 [\text{CN}^-]$). In the denominator, therefore, k_{-4} can be ignored compared to $k_5 [\text{CN}^-]$. With these assumptions equation (22) reduces to equation (23).

$$[\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-} = \frac{k_{-5}}{k_5} \cdot \frac{[\text{Fe}(\text{CN})_5\text{OH}^{3-}][\text{L}^{n-}]}{[\text{CN}^-]} \quad (23)$$

Substitution of concentration of $[\text{FeL}(\text{OH})(\text{CN})_4]^{(n+2)-}$ from equation (23) in equation (20) gives equation (24)

$$\text{rate} = -d[\text{Fe}(\text{CN})_5\text{OH}^{3-}]/dt = k_r[\text{Fe}(\text{CN})_5\text{OH}^{3-}][\text{L}^{n-}]/[\text{CN}^-] \quad (24)$$

where $K_5^{-1} = k_{-5}/k_5$ and $k_r = k_{-4}K_5^{-1}$.

This expression is in conformity with the observed rate law for the reverse reaction given in equation (7).

The magnitude of activation parameters also support the proposed mechanism. A lower value of enthalpy of activation (ΔH^\ddagger) and a large decrease of entropy of activation (ΔS^\ddagger) in the forward reactions compared to the reverse reactions (Table II.7), for both the systems investigated, point to an associative mechanism rather than a dissociative one and are consistent with the rate-determining step (equation 16) proposed in the mechanistic scheme given in equations (13-17).

The pseudo-first-order plots for the forward reactions show positive and negative deviations from linearity at high and low cyanide concentration respectively (not shown). If this were due to reversibility, the deviations would have been negative only. Also, the occurrence of reverse reaction is ruled out due to high stability of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ compared to that of $\text{FeL}(\text{OH})$. Another

reason is the presence of high concentration of cyanide in the reaction mixture which would prevent the reverse reaction to proceed to any appreciable extent. Therefore, it is reasonable to assume that some other reaction(s) are taking place in the system.

A repetitive scan of the reaction mixtures (Fig. II.9 and Fig. II.10) at suitable intervals gives a wealth of information and evidence for all the reactions taking place in these systems. The reactants are $[\text{FeL}(\text{OH})]$ and $[\text{FeL}(\text{OH})_2]$ for HPDTA and HIDA systems respectively. The repetitive scans show an increase in the height of the 395 nm peak (λ_{max} of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$) at the beginning of the reaction, but as the concentration of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ increases and attains $\sim 70\%$ of the theoretical maximum value, the peak height starts decreasing. This shows that $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ starts reacting with excess cyanide to produce $[\text{Fe}(\text{CN})_6]^{3-}$. This is further supported by the appearance of two new peaks at about 300 nm and 257 nm in the UV region due to formation of $[\text{Fe}(\text{CN})_6]^{3-}$. The height of peaks at 300 nm and 257 nm start increasing followed by a decay of the same in the later part of reaction. This is due to the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ by L^{n-} released in the first stage. In the later part of reaction the peak heights due to $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and L^{n-} go down which is in agreement with the proposals given above.

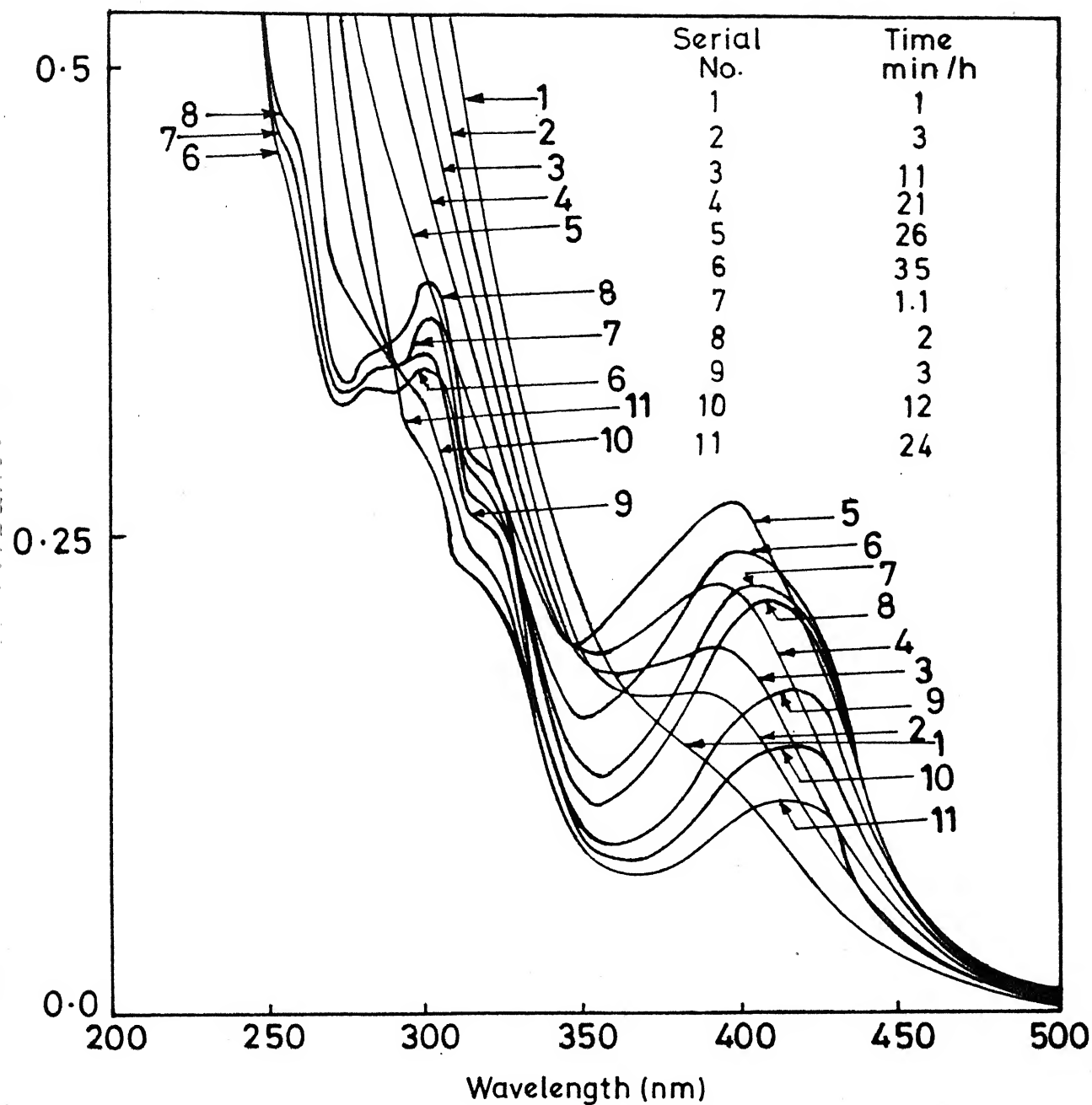


Fig.II.9 Repetitive scan of the reaction mixture during a typical kinetic run at 25°C, $[\text{FeHPDTA}(\text{OH})^{2-}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{CN}^-] = 9 \times 10^{-2} \text{ M}$, $\text{pH} = 10.5$ and $I = 0.1 \text{ M}$ (NaClO_4).

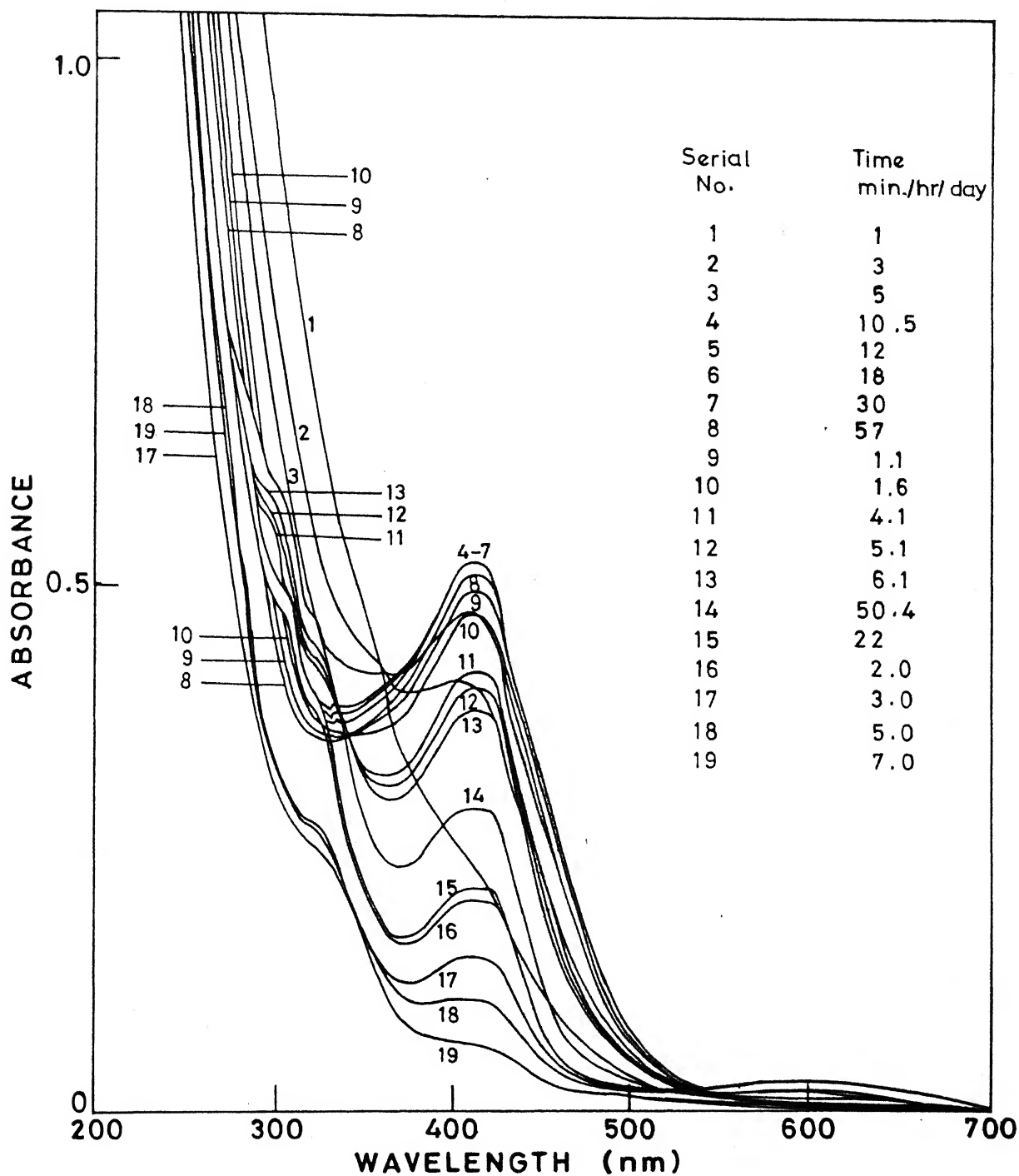
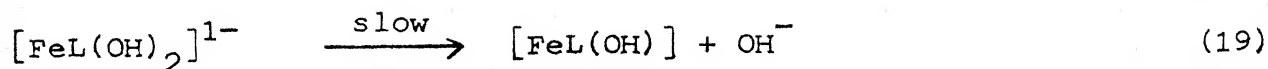


Fig. II.10 Repetitive scan of the reaction mixture during a typical kinetic run; $[\text{Fe HIDA}(\text{OH})_2] = 5 \times 10^{-4} \text{ M}$, $[\text{CN}^-]_{\text{T}} = 2 \times 10^{-2}$, $\text{pH} = 9.5 \pm 0.02$, $I = 0.1 \text{ M} (\text{NaClO}_4)$ and $\text{temp.} = 25^\circ \text{C}$.

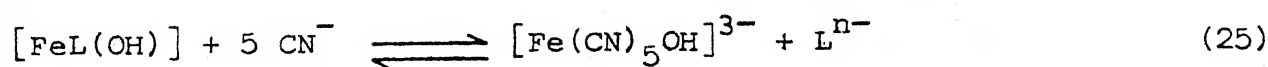
Alkaline hexacyanoferrate(III) is a one-electron oxidising agent and is known to oxidise many aminocarboxylates viz. EDTA, IDA and NTA.⁴⁰ Kinetics of oxidation of DTPA by $[\text{Fe}(\text{CN})_6]^{3-}$ has been investigated before in our laboratory.⁴¹ All these oxidation reactions have been found to follow the same mechanism. So it is expected that oxidations of HPDTA and HIDA should also fall in line and have, therefore, not been pursued. The first stage of the reaction ($[\text{FeL}(\text{OH})]^{2-n}$) has been found to be slow compared to the other two stages of the reaction. But in the case of HIDA system it is found to be very slow compared to oxidation reactions of $[\text{Fe}(\text{CN})_6]^{3-}$ with other aminocarboxylates in their respective systems.

The positive ammonium molybdate and thorium nitrate tests⁴² for the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ at the end of the reaction and a negative test at the beginning confirm that the oxidation of L^{n-} by the $[\text{Fe}(\text{CN})_6]^{3-}$ formed during the second stage of reaction, does take place eventually.

So the overall reaction of $[\text{FeL}(\text{OH})]^{2-n}$ with excess of cyanide can be divided into three distinguishable stages. The sequence of these three stages of reactions may be written as First stage:

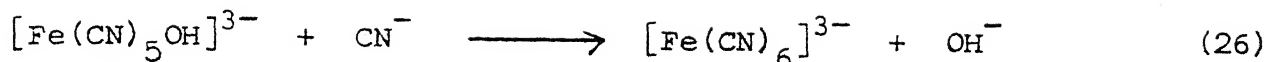


for L = HIDA only

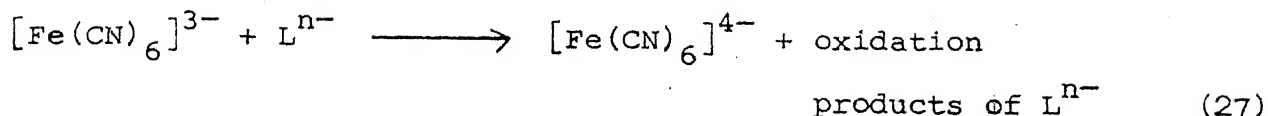


(in 5 steps according to eqns. 13-17)

Second stage:



Third stage:

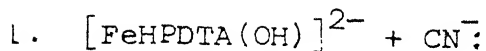


The rate constants for the 1st & 2nd stages are summarized in Table II.8.

The existence of an isosbestic point at 355 nm during the course of reaction (Fig.9 and 10) shows the conversion of $[\text{FeL}(\text{OH})]^{2-n}$ to $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$. A second isosbestic point around 320 nm in both the systems corresponds to a coexistence of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$.

The occurrence of isosbestic points (preferably two and more) during a repetitive scan of a reaction, strongly suggests that the original reactant is being replaced by one or more products and that these are always present in a strictly constant ratio.⁴³ An illustration of this is seen in the occurrence of seven isosbestic points in the relatively fast reaction of HgTPP with Zn(II) in pyridine (TPP = tetraphenylporphyrin).⁴⁴ These seven isosbestic points show that HgTPP converts to ZnTPP without formation of appreciable amounts of free TPP base which has different spectrum

Table II.8. Rate constants for various stages of the reactions;
Conditions as given in Table II.3¹ and Table II.6³.

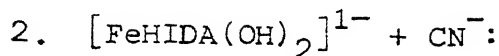


$$k_4 = 1.07 \times 10^{-2}, \text{ M}^{-1} \text{ s}^{-1}$$

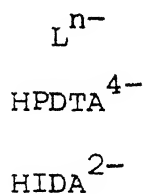
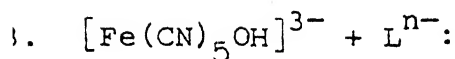
$$k_4 K_3 = 1.23 \times 10^{-1}, \text{ M}^{-2} \text{ s}^{-1}$$

$$k_4 K_3 K_2 = 1.80, \text{ M}^{-3} \text{ s}^{-1}$$

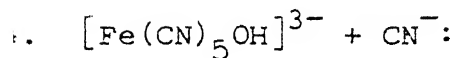
$$k_4 K_3 K_2 K_1 = 1.12 \times 10^{10}, \text{ M}^{-4} \text{ s}^{-1}$$



$$k_4 = 2.16 \times 10^{-2}, \text{ M}^{-1} \text{ s}^{-1}$$



$$\begin{array}{l} k_r (=K_5^{-1} k_{-4}), \text{ s}^{-1} \\ (6.1 \pm 0.2) \times 10^{-8} \\ (1.7 \pm 0.1) \times 10^{-8} \end{array}$$



$$k_2 = 3.62 \times 10^{-3}, \text{ M}^{-1} \text{ s}^{-1}$$

$$[\text{Fe}(\text{CN})_5\text{OH}^{3-}] = 1.0 \times 10^{-4} \text{ M}$$

$$[\text{CN}^-] = (2.0-10.0) \times 10^{-2} \text{ M}$$

$$\text{pH} = 10.5, I = 0.25 \text{ M} (\text{NaClO}_4)$$

$$\text{Temp.} = 30 \pm 0.1^\circ \text{C}$$

⁴ Ref. 47.

from either complexes. So it can be assumed that no appreciable amounts of reaction intermediates are formed during the course of reaction.

It is interesting to note that a new low absorption band appears in the later stages of reaction at 600 nm, (λ_{max} of $\text{Fe}_2(\text{CN})_{10}$, $\epsilon = 1600 \text{ M}^{-1}\text{cm}^{-1}$)⁴⁵ in case of HIDA system. This is attributed to the formation of $[\text{Fe}_2(\text{CN})_{10}]^{4-}$ due to dimerization of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$. A scan in the 500 nm - 600 nm region at higher sensitivity showed a small but not insignificant increase in absorption due to formation of the dimer. This is further confirmed by the appearance of a blue colour in later part of reaction. This colour finally fades away, however, because the dimer ultimately converts to the almost colourless $[\text{Fe}(\text{CN})_6]^{3-}$. A dimer formation has also been shown in similar systems studied earlier.

II.5.7 Linear free-energy relationship

An interesting feature of this work is the existence of a linear free energy relationship between rate constants and the stability constants of intermediates of the type $[\text{FeL}(\text{OH})(\text{CN})_x]$ (where $x = 0, 1, 2$ and 3) formed in the five step reaction of FeL ($\text{L} = \text{HPDTA}$) with cyanide ions.

The forward reaction is first order in $[\text{FeL}(\text{OH})]^{2-n}$ and exhibits a variable order dependence in cyanide concentration (always taken in excess). The species $[\text{FeL}(\text{OH})(\text{CN})_x]^{(2-n-x)}$

where $x = 3, 2$ and 1 are the reacting species corresponding to the first, second and third order dependences in cyanide concentrations. The resolved rate constants for the first, second and third order reactions are derived as follows.

$$k_{\text{obs}} = k_4 [\text{FeL}(\text{OH}) (\text{CN})_3^{(n+1)-}] [\text{CN}^-] \quad (28)$$

$$= k_4 K_3 [\text{FeL}(\text{OH}) (\text{CN})_2^{n-}] [\text{CN}^-]^2 \quad (29)$$

$$= k_4 K_3 K_2 [\text{FeL}(\text{OH}) (\text{CN})^{1-n}] [\text{CN}^-]^3 \quad (30)$$

Considering the pre-equilibrium in each step it is evident that the resolved rate constants for first, second and third orders in cyanide are k_4 , $k_4 K_3$ and $k_4 K_3 K_2$ respectively. The reacting species corresponding to the fourth order dependence in cyanide is $[\text{FeL}(\text{OH})]^{2-n}$ itself and the rate constants for the same is $k_4 K_3 K_2 K_1$.

The plots of $\log k'_n$ versus $\log \beta_{\text{lmn}}$ (Fig. II.11 to Fig. II.14) show explicitly the relationship between k'_n 's ($k'_1 = k_4 K_3 K_2 K_1$, $k'_2 = k_4 K_3 K_2$, $k'_3 = k_4 K_3$ and $k'_4 = k_4$) and the respective overall stability constants (β_{lmn}) viz. β_{110} , β_{111} , β_{112} and β_{113} of the intermediates, reacting in the respective steps in order, for different ligand systems viz. DTPA, HEDTA and EDTA.⁴⁶ HPDTA also fits in to these linear plots though with some deviation (Fig. II.11 to Fig. II.13). The rate of exchange of HPDTA on $[\text{FeHPDTA}(\text{OH})]^{2-}$

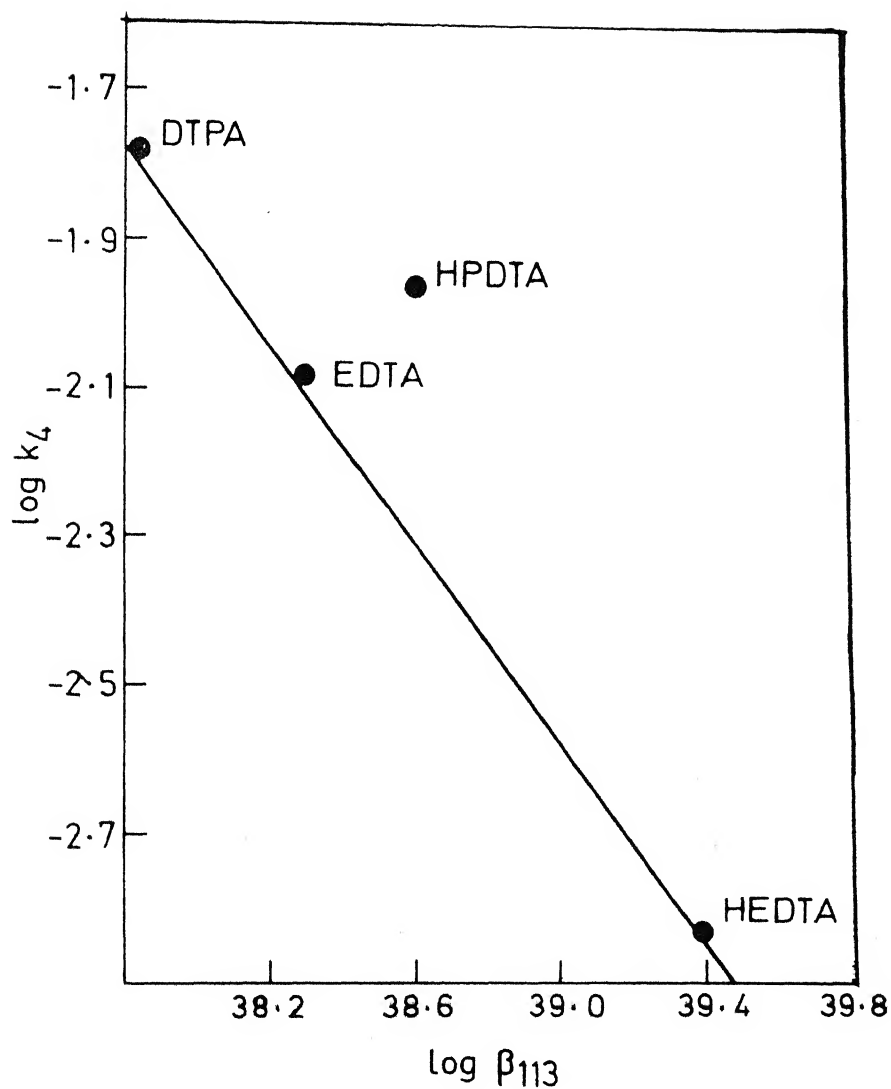


Fig.II.11 Plot of $\log(k_4)$ versus \log (overall stability constants) of $[\text{FeL}(\text{OH})(\text{CN})_3]^{-(n+1)}$ intermediates i.e. $\log \beta_{113}$

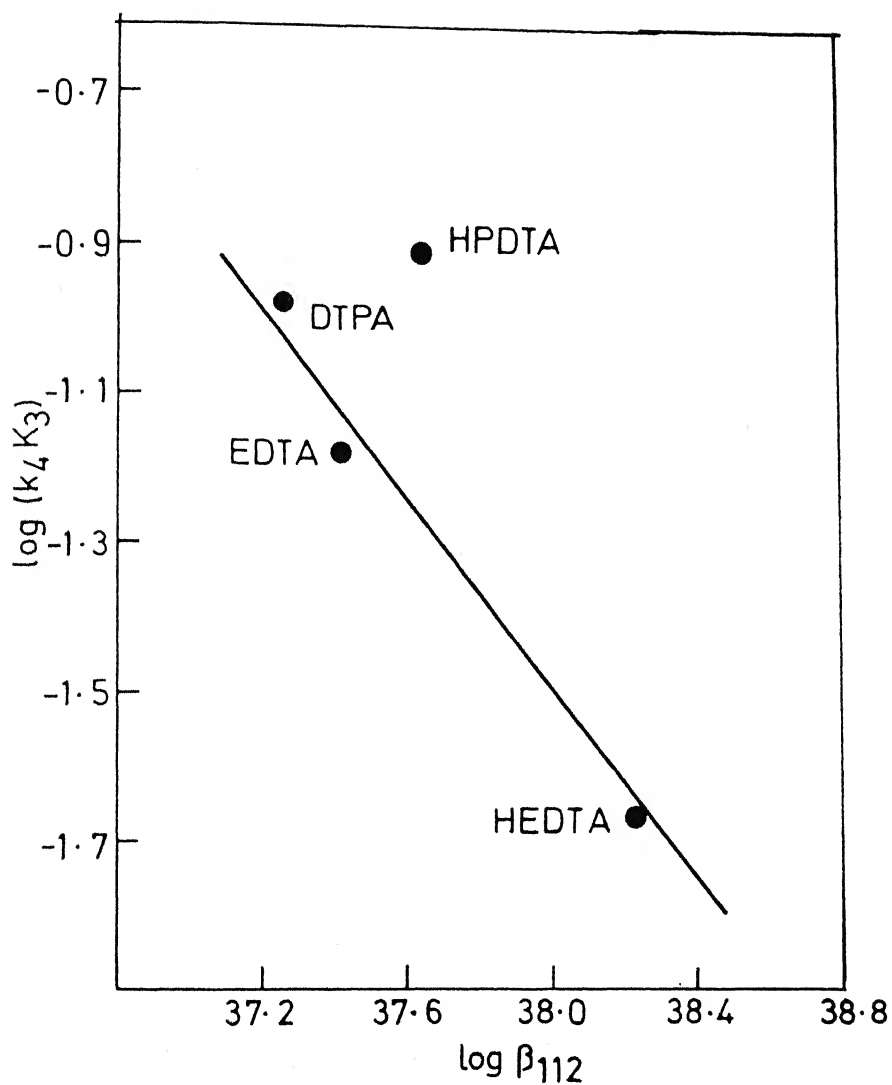


Fig.II.12 Plot of $\log(k_4 K_3)$ versus \log (overall stability constants) of $[\text{FeL}(\text{OH})(\text{CN})_2]^{-n}$ intermediates i.e. $\log \beta_{112}$

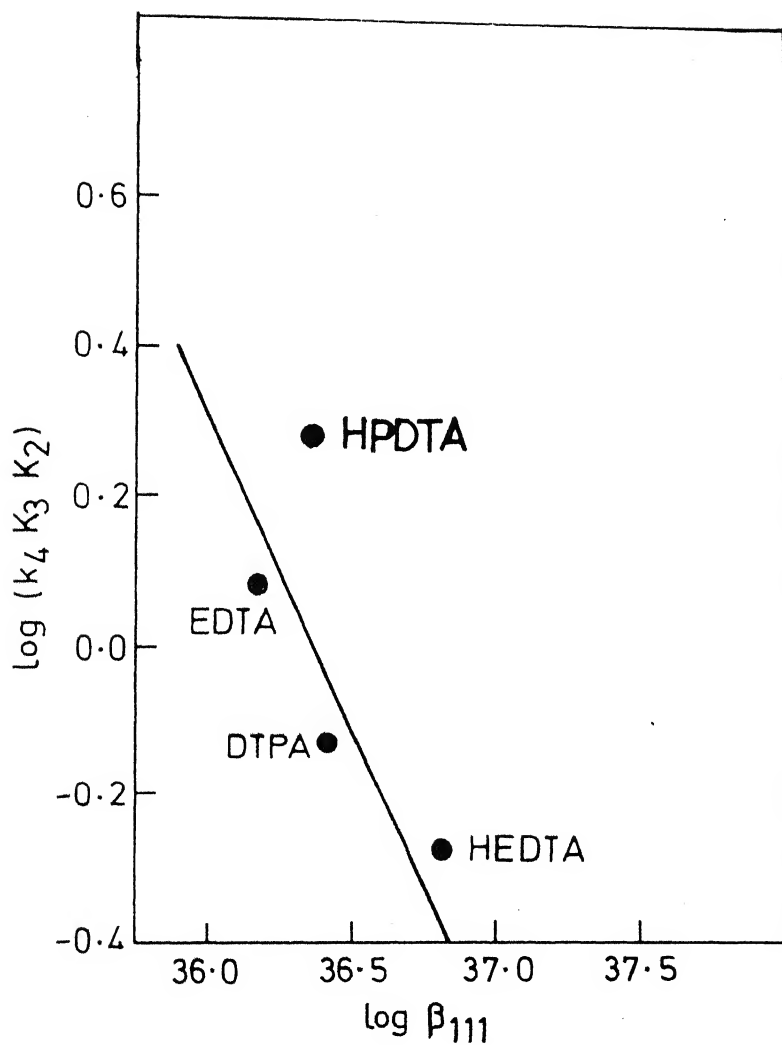


Fig.II.13 Plot of $\log (k_4 K_3 K_2)$ versus \log (overall stability constants) of $[\text{FeL}(\text{OH})(\text{CN})]^{1-n}$ intermediates i.e. $\log \beta_{112}$.

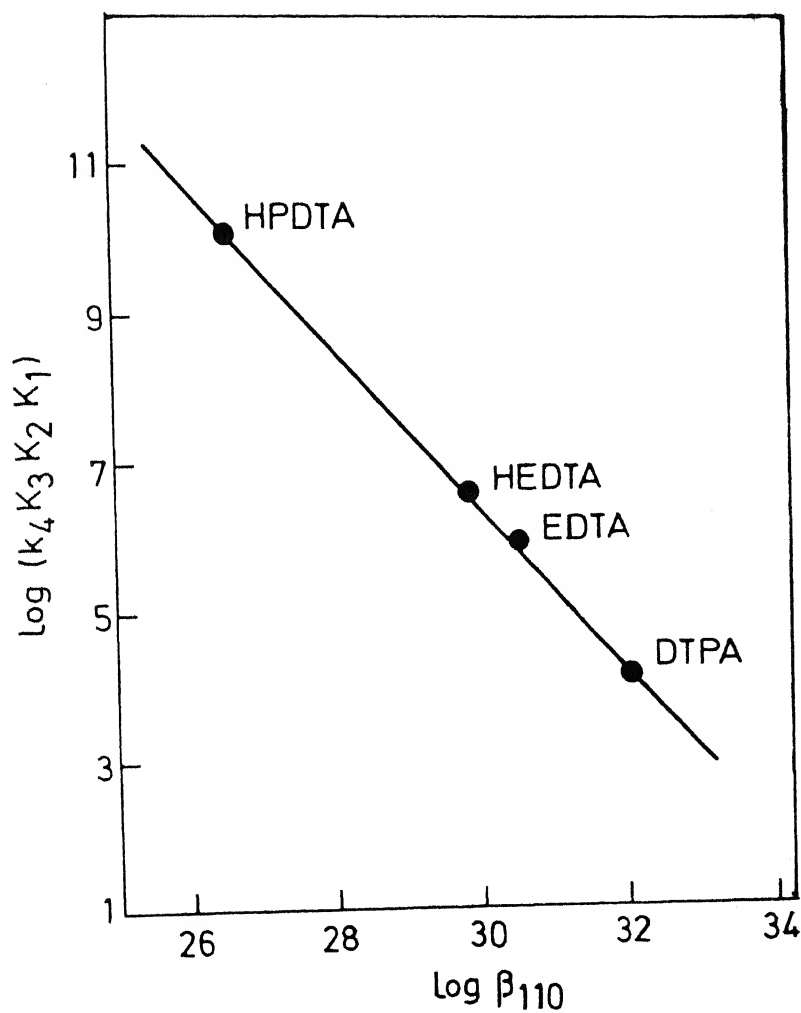


Fig.II.14 Plot of $\log (k_4 K_3 K_2 K_1)$ versus \log (overall stability constant) of $[\text{FeLOH}]^{2-n}$ complexes i.e. $\log \beta_{110}$

is found to be faster than the expected rate. This deviation from expected reactivities can be attributed to the requirements of the hydroxyl group and its effect on the course of reaction. The presence of the electron withdrawing hydroxyl group results in weakening of the metal-nitrogen bond and thus increase in the lability of the metal complex.

The values for β_{lmn} (overall stability constants of the intermediate reacting species) in terms of β_{110} are formulated from expression (31) to (34).

$$\beta_{113} = K_{\text{FeL(OH)(CN)}_3} = K_3 K_2 K_1 \beta_{110} \quad (31)$$

$$\beta_{112} = K_{\text{FeL(OH)(CN)}_2} = K_1 K_2 \beta_{110} \quad (32)$$

$$\beta_{111} = K_{\text{FeL(OH)(CN)}} = K_1 \beta_{110} \quad (33)$$

$$\text{where } \beta_{110} = K_{\text{FeL(OH)}} \quad (34)$$

Another linear free-energy relationship has been verified between the rate constants, k_n' with overall stability constants β_{lmn} of the intermediates viz. FeL(OH)(CN)_3 , FeL(OH)(CN)_2 , FeL(OH)(CN) and lastly with the initial reacting species viz. FeL(OH) , for each individual aminocarboxylate reaction. A linear plot for HPDTA reaction system is given in Fig. II.15. In other systems like DTPA, HEDTA and EDTA (not shown), studied earlier in

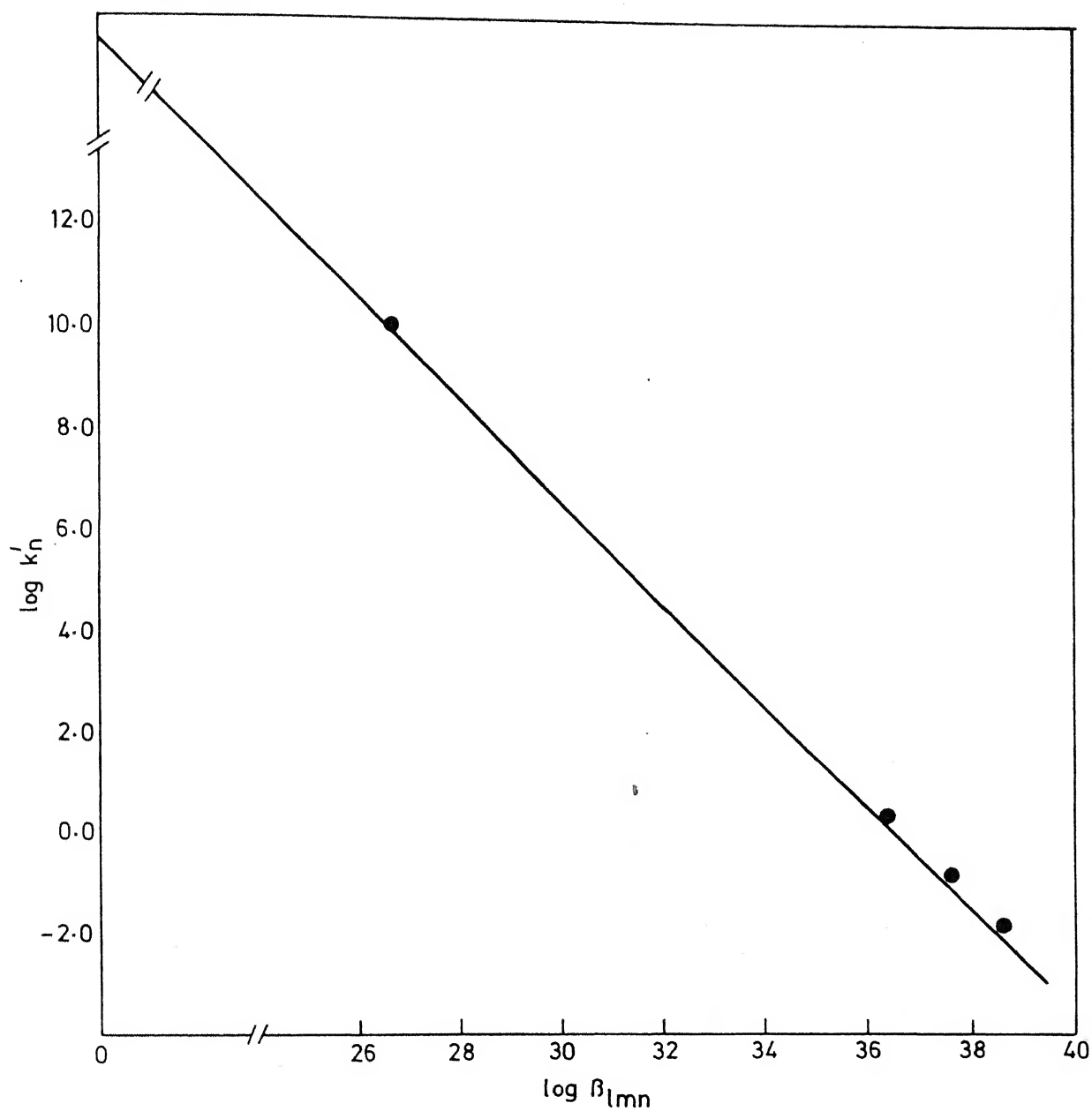


Fig.II.15 Plot of $\log k'_n$ versus $\log \beta_{lmn}$ for $[\text{FeHPDTA}(\text{OH})]^{2-} - \text{CN}^-$ reaction.

our laboratory⁴⁶, the individual plots obtained for each amino-carboxylates have almost equal slopes but have different intercepts.²¹ The data for overall stability constants of the intermediates along with first, second, third and fourth order rate constants are given in Table II.9. Data for HIDA which shows only zero and first order dependences in cyanide can not be plotted in this manner.

Interpretation of data:

It has been shown in the foregoing that

$$\begin{aligned}\text{Forward rate} &= k_4 [\text{FeL}(\text{OH})(\text{CN})_3^{(n+1)-}] [\text{CN}^-] \\ &= k_4 K_3 K_2 K_1 [\text{FeL}(\text{OH})^{2-n}] [\text{CN}^-]^4\end{aligned}\quad (35)$$

$$\begin{aligned}\text{Reverse rate} &= k_{-4} [\text{FeL}(\text{OH})(\text{CN})_4^{(n+2)-}] \\ &= k_{-4} K_5^{-1} [\text{Fe}(\text{CN})_5 \text{OH}^{3-}] [\text{L}^{n-}] / [\text{CN}^-]\end{aligned}\quad (36)$$

Equating both forward and reverse rates at equilibrium one gets,

$$k_4 K_3 K_2 K_1 [\text{FeL}(\text{OH})^{2-n}] [\text{CN}^-]^4 = k_{-4} K_5^{-1} [\text{Fe}(\text{CN})_5 \text{OH}^{3-}] [\text{L}^{n-}] / [\text{CN}^-] \quad (37)$$

$$\text{or } k_4 K_3 K_2 K_1 = \frac{k_{-4} K_5^{-1} [\text{Fe}(\text{CN})_5 \text{OH}^{3-}] [\text{L}^{n-}]}{[\text{CN}^-]^5 [\text{FeL}(\text{OH})^{2-n}]} \quad (38)$$

multiplying and dividing by $[\text{Fe}^{3+}][\text{OH}^-]$ in numerator and denominator of R.H.S. of equation (38) one gets

Table II.9. Evaluation of overall stability constants (β_{lmn}) of the intermediates in the reaction of the HPDTA with cyanide and the corresponding rate constants (k'_n) for individual steps.

Reacting species	Rate constants	$\log \beta_{lmn}$ (β_{lmn} = overall stability const.)	K Stepwise stability constants
$[\text{FeL}(\text{OH})]^{2-n}$	$k_4 k_3 k_2 k_1 = 1.12 \times 10^{10}, \text{M}^{-4} \text{s}^{-1}$	26.65	$K_1 = 5.9 \times 10^9$
$[\text{FeL}(\text{OH})\text{CN}]^{1-n}$	$k_4 k_3 k_2 = 1.90, \text{M}^{-3} \text{s}^{-1}$	36.40	$K_2 = 15.8$
$[\text{FeL}(\text{OH})(\text{CN})_2]^{n-}$	$k_4 k_3 = 1.2 \times 10^{-1}, \text{M}^{-2} \text{s}^{-1}$	37.61	$K_3 = 11.2$
$[\text{FeL}(\text{OH})(\text{CN})_3]^{(n+1)-}$	$k_4 = 1.07 \times 10^{-2}, \text{M}^{-1} \text{s}^{-1}$	38.6	

$$k_4 K_3 K_2 K_1 = \frac{k_{-4} K_5^{-1} [\text{Fe}(\text{CN})_5 \text{OH}^{3-}] [\text{L}^{n-}] [\text{Fe}^{3+}] [\text{OH}^-]}{[\text{Fe}^{3+}] [\text{CN}^-]^5 [\text{OH}^-] [\text{FeL}(\text{OH})^{2-n}]} \quad (39)$$

$$= k_{-4} K_5^{-1} \beta_5 / K_{\text{FeL}(\text{OH})} \quad (40)$$

$$\text{where } \beta_5 = \frac{[\text{Fe}(\text{CN})_5 \text{OH}^{3-}]}{[\text{Fe}^{3+}] [\text{OH}^-] [\text{CN}^-]^5} \quad (41)$$

$$\text{and } K_{\text{FeL}(\text{OH})} = \frac{[\text{FeL}(\text{OH})^{2-n}]}{[\text{Fe}^{3+}] [\text{L}^{n-}] [\text{OH}^-]} \quad (42)$$

From equation (40) one gets,

$$K_1 = \frac{k_r \beta_5}{K_{\text{FeL}(\text{OH})} \cdot k_4 K_3 K_2} \quad (43)$$

$$\text{where } k_r = k_{-4} K_5^{-1} \quad (44)$$

The beauty of this expression (equation 43) is that one can calculate a value for K_1 which has not been possible by a kinetic procedure because the expected fourth order dependence in cyanide has not been experimentally observed (*vide infra*). This also enables one to determine the fourth order rate constant $k_4 K_3 K_2 K_1$ from a combination of experimental rate data and equation (43). Table II.8 includes the fourth order rate constant for HPDTA system. The β_5 of $[\text{Fe}(\text{CN})_5 \text{OH}]^{3-}$ has been determined spectrophotometrically earlier in our laboratory.³⁰

Rearranging equation (43) and taking logarithm of both sides one gets equations (45) to (48).

$$\log (k_4 K_3 K_2 K_1) = \log (k_r \beta_5) - \log \beta_{110} \quad (4^{\text{th}} \text{ order}) \quad (45)$$

$$\log (k_4 K_3 K_2) = \log (k_r \beta_5) - \log \beta_{111} \quad (3^{\text{rd}} \text{ order}) \quad (46)$$

$$\log (k_4 K_3) = \log (k_r \beta_5) - \log \beta_{112} \quad (2^{\text{nd}} \text{ order}) \quad (47)$$

$$\log k_4 = \log (k_r \beta_5) - \log \beta_{113} \quad (1^{\text{st}} \text{ order}) \quad (48)$$

Equations (45-48) predict an inverse dependence of $k_4 K_3 K_2$ on β_{111} ; of $k_4 K_3$ on β_{112} and of k_4 on β_{113} respectively with a slope equal to -1. This has been found to be the case as shown in Fig. II.11 to Fig. II.13.

Equations (45-48) can be rewritten in the form of a general equation (49).

$$\log k'_n = m \log \beta_{lmn} + C \quad (49)$$

where $m(= -1)$ is the slope and $C(= \log k_r \beta_5)$ is a constant. This general equation has been verified for DTPA, HEDTA and EDTA and lastly for HPDTA system.

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CHAPTER III

KINETIC AND MECHANISTIC STUDY ON SUBSTITUTION OF AMINOCARBOXYLATES COORDINATED TO Mn(III) CENTRE BY CYANIDE IONS

ABSTRACT

Kinetics and mechanism of the reaction of cyanide ions with complexes of manganese(III) with trans-1,2-diaminocyclohexanetetraacetate anion (CYDTA^{4-}), hydroxyethylethylenediaminetriacetate anion (HEDTA^{3-}) and ethylenediaminetetraacetate anion (EDTA^{4-}) have been studied spectrophotometrically at temp. = 25°C , $I = 0.1\text{--}0.25\text{M}$ (NaClO_4) and $\text{pH} = 9.5\text{--}10.5$. The forward reaction, always carried out in presence of excess cyanide, is found to be first order with respect to the metal complex and exhibits a variable order ranging from two to one in case of $\text{MnEDTA} - \text{CN}^-$ reaction but only first order dependence in cyanide in the case of CYDTA and HEDTA reaction systems.

The kinetics of reverse reaction i.e., the reaction between $[\text{Mn}(\text{CN})_6]^{3-}$ and EDTA^{4-} , CYDTA^{4-} and HEDTA^{3-} (always taken in large excess) have also been followed spectrophotometrically. In all

the three systems, the reactions follow a first-order kinetics each in $[\text{Mn}(\text{CN})_6^{3-}]$ and the respective ligand concentration and an inverse-first-order dependence in $[\text{CN}^-]$. A six-step mechanism is proposed for the forward reaction where the fifth step is the rate-determining one. The pH dependences, ionic strength dependences and temperature dependences have also been studied for all the three systems and rationalized.

II.2 Introduction

The kinetics of substitution of multidentate ligands from their complexes of metal ions by monodentate or multidentate ligands has been an active area of research for some decades. Such studies have thrown valuable light on the mechanistic pathways of this important class of reactions. The formation of tetracyanonickelate(II) from the reaction of aminopolycarboxylatonickelate(II) with cyanide ions has been studied extensively.¹⁻¹¹ In recent years, substitution reactions of aminocarboxylates on $[\text{FeL}(\text{OH})]^{2-n}$ complexes by cyanide ions¹²⁻¹⁷ where L^{n-} is EDTA^{4-} ,¹² HEDTA^{3-} ,¹³ DTPA^{5-} , PDTA^{4-} ,¹⁴ HPDTA^{4-} ,¹⁶ TTHA^{6-} and HIDA^{2-} ¹⁷ have been investigated. The mechanism proposed for all these systems involves a five step reaction sequence leading to the formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$.

The exchange reactions on Mn(III) have received but little attention except for a single earlier report on $[\text{MnCYDTA}(\text{OH})]^{2-}-\text{CN}^-$ system by Hamm and Templeton.¹⁸ A similar system viz. $[\text{MnEDTA}(\text{OH})]^{2-}-\text{CN}^-$ has been investigated in our laboratory and a different tentative mechanism for the same has been suggested.¹⁹ This was followed by a more detailed study on two other similar systems in order to confirm the mechanism proposed by us.²⁰ The $[\text{MnCYDTA}(\text{OH})]^{2-}-\text{CN}^-$ system, which had been investigated earlier by Hamm and Templeton¹⁸, has been reinvestigated by us in the light of our results on $[\text{MnEDTA}(\text{OH})]-\text{CN}^-$ ^{19,20} and $[\text{MnHEDTA}(\text{OH})]-\text{CN}^-$ ²¹ systems and is also shown to follow the same mechanism. Thus the proposed mechanism appears to be quite general for this class of reactions.

To the best of our knowledge, this is the first comprehensive study on ligand substitution reactions of aminopolycarboxylato-manganate(III) complexes.

III.3 Experimental Section

$\text{Na}_2\text{H}_2\text{CYDTA}$ (AR, BDH), HEDTA (AR, SIGMA, USA), $\text{Na}_2\text{H}_2\text{EDTA}$ (AR, BDH), $\text{Mn}(\text{CH}_3\text{COO})_3$ (Aldrich, USA), NaCN (May and Baker, England), NaClO_4 (E. Merck, Germany) have been used in this study. $\text{K}_3[\text{Mn}(\text{CN})_6]$ crystals have been prepared by a literature method.²² The sodium cyanide solutions are standardized argentometrically.²³ For the preparation of complexes, ligands are always taken in 20%

excess over the stoichiometric requirement. The concentration of Mn^{3+} in the complex is determined by an iodometric method.²⁴ NaOH or HClO_4 is used to maintain pH at any desired value.

It is ensured that all reagents are free from reducing substances. In particular, the dilute solution of NaOH, used for adjusting the pH, is tested each time before use by addition of a drop of 0.02M potassium permanganate. The absence of green colour shows absence of any reducing matter in the solution. Millipored triple distilled water is used throughout the experimental work for preparation of solutions and rinsing of glass ware.

A double beam Shimadzu spectrophotometer Model UV-240, equipped with a circulatory arrangement for thermostating the cell compartment, is used for measuring absorbances and for spectral scans of the reaction mixtures. An ultracryostat model 2 NBE (VED Kombinat, GDR) is used for maintenance of temperature at any desired value before mixing the reactants. All pH measurements have been made on an Elico digital pH meter model LI-120 using BDH buffers for standardization.

III.4 Kinetic measurements

Mn(III) forms mononuclear 1:1 complexes with CYDTA^{4-} ,²⁴ HEDTA^{3-} ,²⁴ and EDTA^{4-} ²⁵ in the chosen experimental conditions.

The names and structures of these ligands are given in Table III.1. The protonation constants and the stability constants of these

Table III.1. Names and structures of aminopolycarboxylates

L^{n-}	Name	Structure
	Trans-1,2-diaminocyclohexane N,N,N',N'-tetraacetate anion.	
	Hydroxyethylethylenediaminetriacetate anion.	
	Ethylenediaminetetraacetate anion.	

complexes, which are believed to exist in a heptacoordinated form in the solution phase,^{24,25} are given in Table III.2. The major reactant species are the respective hydroxo species of the complexes above $\text{pH} > 8$, $\text{pH} > 6^{31}$ and $\text{pH} > 6^{31}$ respectively for these systems in order while the cyanide is present as HCN ($\text{pK}_a = 9.2$)³² and CN^- . The spectra of all the three hydroxy species are given in Fig. III.1.

III.5 Kinetics of Forward Reaction

The reaction between $[\text{MnL}(\text{OH})]^{2-n}$ and cyanide ions is thermodynamically favoured (stability constants given in Table III.2B) and followed spectrophotometrically. The reaction conditions are: $\text{pH} = 10.5 \pm 0.02$, $I = 0.25\text{M}(\text{NaClO}_4)$, $\lambda = 448 \text{ nm}$ (λ_{max} $[\text{MnCYDTA}(\text{OH})]$, $\epsilon = 329 \text{ M}^{-1}\text{cm}^{-1}$); $\text{pH} = 9.5 \pm 0.02$, $I = 0.1\text{M}(\text{NaClO}_4)$, $\lambda = 449 \text{ nm}$ (λ_{max} $[\text{MnHEDTA}(\text{OH})]$, $\epsilon = 312 \text{ M}^{-1}\text{cm}^{-1}$) and $\text{pH} = 10.0 \pm 0.02$, $I = 0.1\text{M}(\text{NaClO}_4)$, $\lambda = 325 \text{ nm}$ (λ_{max} $[\text{Mn}(\text{CN})_6]^{3-}$, $\epsilon = 3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$)³³ for CYDTA, HEDTA and EDTA systems respectively. The forward reactions are carried out in presence of adequate excess of cyanide under pseudo-first-order conditions.

In the reaction of ethylenediaminetetraacetatomanganate(III) complex with cyanide ion, the former also absorbs at the chosen wavelength (325 nm). So corrections are applied for absorbance of this species. An expression (2) is derived for calculation of concentration of A based on reaction (1).

Table III.2.A. Protonation constants of aminopolycarboxylates at 25°C ($\log K_H$), $I = 0.1M(NaClO_4/KNO_3)$.

L^{n-}	HL	H_2L	H_3L	H_4L	Ref.
CYDTA ⁴⁻	12.4	6.15	3.53	2.42	26,27
HEDTA ³⁻	9.81	5.41	2.72	-	28
EDTA ⁴⁻	10.34	6.24	2.75	2.07	28

B. Stability constants for aminocarboxylato-manganate(III) complexes ($\log K$) at 25°C, $I = 0.2M(NaClO_4)$.

L^{n-}	MnL	Ref.
CYDTA ⁴⁻	28.9	29
HEDTA ³⁻	22.7	29
EDTA ⁴⁻	24.9	30

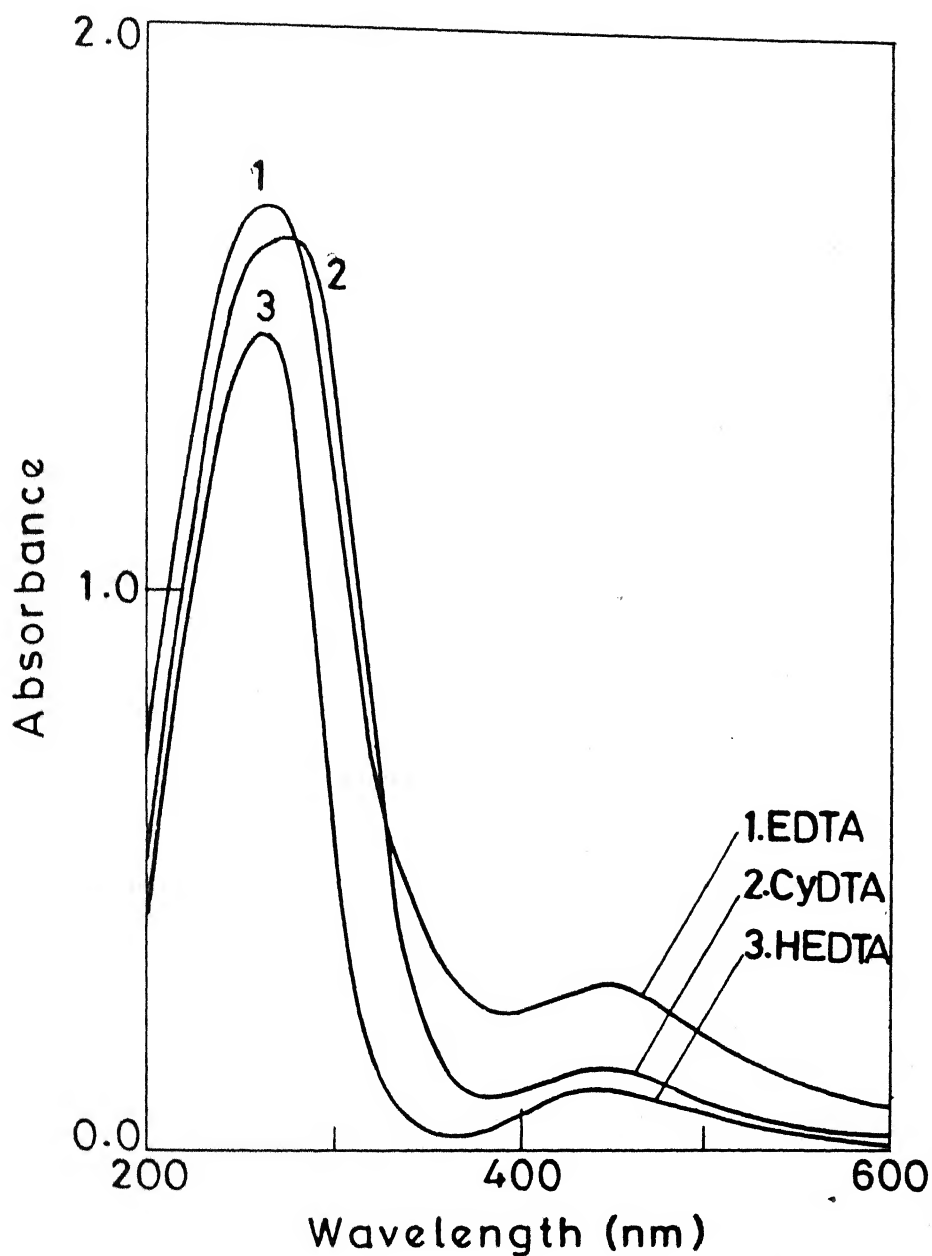
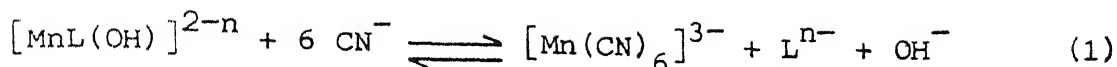


Fig. III.1 Absorption spectra of $[\text{MnL}(\text{OH})]^{2-n}$ complexes; $[\text{MnL}(\text{OH})]^{2-n} = (1.0 \sim 6.0) \times 10^{-4} \text{ M}$, $\text{pH} = 10.0$, $\text{temp.} = 25^\circ \text{C}$.



$$C_A = (\epsilon_B C_A^0 - A_t) / (\epsilon_B - \epsilon_A) \quad (2)$$

where $A = [\text{MnL}(\text{OH})]^{2-n}$, $B = [\text{Mn}(\text{CN})_6]^{3-}$, ϵ_A and ϵ_B are their respective molar absorbitivities and C_A^0 is the initial concentration of $[\text{MnL}(\text{OH})]^{2-n}$.

Pseudo-first-order plots are obtained in each system over about 60-70% of the reaction. The pseudo-first-order rate constants are calculated from the slopes of plots of $\log C_A$ versus time 't', where C_A is the concentration of $[\text{MnL}(\text{OH})]^{2-n}$ at any time t. The values of rate constants are compiled in Table III.3 for all the three systems.

The reaction exhibits first-order dependence in cyanide in case of CYDTA and HEDTA reactions whereas a variable order dependence in $[\text{CN}^-]$, one at high and two at low cyanide concentration, is observed in case of EDTA. A plot of $\log k_{\text{obs}}$ versus $\log [\text{CN}^-]_T$ for all the three systems are given in Fig. III.2.

This is for the first time that a variable order dependence on cyanide has been observed in ligand substitution reactions of $[\text{MnL}(\text{OH})]^{2-n}$ by cyanide ions ($\text{L}^{n-} = \text{EDTA}^{4-}$) though similar observations have been made on $[\text{NiL}]^{2-n} - \text{CN}^{-1-11}$ and $[\text{FeL}(\text{OH})]^{2-n} - \text{CN}^{-12-17}$ reactions in earlier studies. An experimental rate expression formulated for the forward reactions is given in equation (3).

Table III.3. Effect of $[\text{CN}^-]$ on formation of $[\text{Mn}(\text{CN})_6]^{3-}$ from amino-carboxylatomanganate(III) complexes in presence of cyanide ions at 25°C .

A. $[\text{MnCYDTA}(\text{OH})^{2-}] = (1.5-4.0) \times 10^{-4}\text{M}$

$[\text{CN}^-]_{\text{T}}, 10^2\text{M}$	$k_{\text{obs}}, \text{s}^{-1}, 10^4$	$k_{\text{f}} = k_{\text{obs}}/[\text{CN}^-], \text{M}^{-1}\text{s}^{-1}, 10^3$
8.0	2.95	3.68
9.0	3.55	3.94
10.0	3.62	3.62
15.0	5.01	3.34
20.0	6.82	3.41

$$k_{\text{f}}(\text{av}) = (3.60 \pm 0.21) \times 10^{-3}, \text{M}^{-1}\text{s}^{-1}$$

B. $[\text{MnHEDTA}(\text{OH})^{1-}] = (1.2-2.0) \times 10^{-4}\text{M}$

6.0	4.80	8.00
7.0	4.92	7.02
8.0	7.08	8.85
9.0	8.15	9.06
10.0	8.81	8.81

$$k_{\text{f}}(\text{av}) = (8.35 \pm 0.76) \times 10^{-3}, \text{M}^{-1}\text{s}^{-1}$$

A. pH = 10.5 ± 0.02 , I = 0.25M(NaClO_4).

B. pH = 9.5 ± 0.02 , I = 0.1M(NaClO_4).

...contd.

Table III.3(contd.).

c. $[\text{MnEDTA}(\text{OH})^{2-}] = (2.0-4.2) \times 10^{-4} \text{ M}$

$[\text{CN}^-], 10^2 \text{ M}$ $k_{\text{obs}}, \text{ s}^{-1}$ $k_f = k_{\text{obs}} / [\text{CN}^-]^x$

2.5	3.60×10^{-4}	5.76×10^{-1}
3.75	8.16×10^{-4}	5.80×10^{-1}
4.1	1.03×10^{-3}	6.13×10^{-1}
4.6	1.15×10^{-3}	5.44×10^{-1}
5.0	1.39×10^{-3}	5.60×10^{-1}

$$k_f(\text{av}) = (5.75 \pm 0.23) \times 10^{-1}, \text{ M}^{-2} \text{ s}^{-1}$$

6.0	1.50×10^{-3}	2.5×10^{-2}
7.0	1.62×10^{-3}	2.31×10^{-2}
8.0	1.75×10^{-3}	2.19×10^{-2}
10.0	2.13×10^{-2}	2.13×10^{-2}

$$k_f(\text{av}) = (2.28 \pm 0.14) \times 10^{-2}, \text{ M}^{-1} \text{ s}^{-1}$$

c. $\text{pH} = 10.0 \pm 0.02, I = 0.1 \text{ M}(\text{NaClO}_4).$

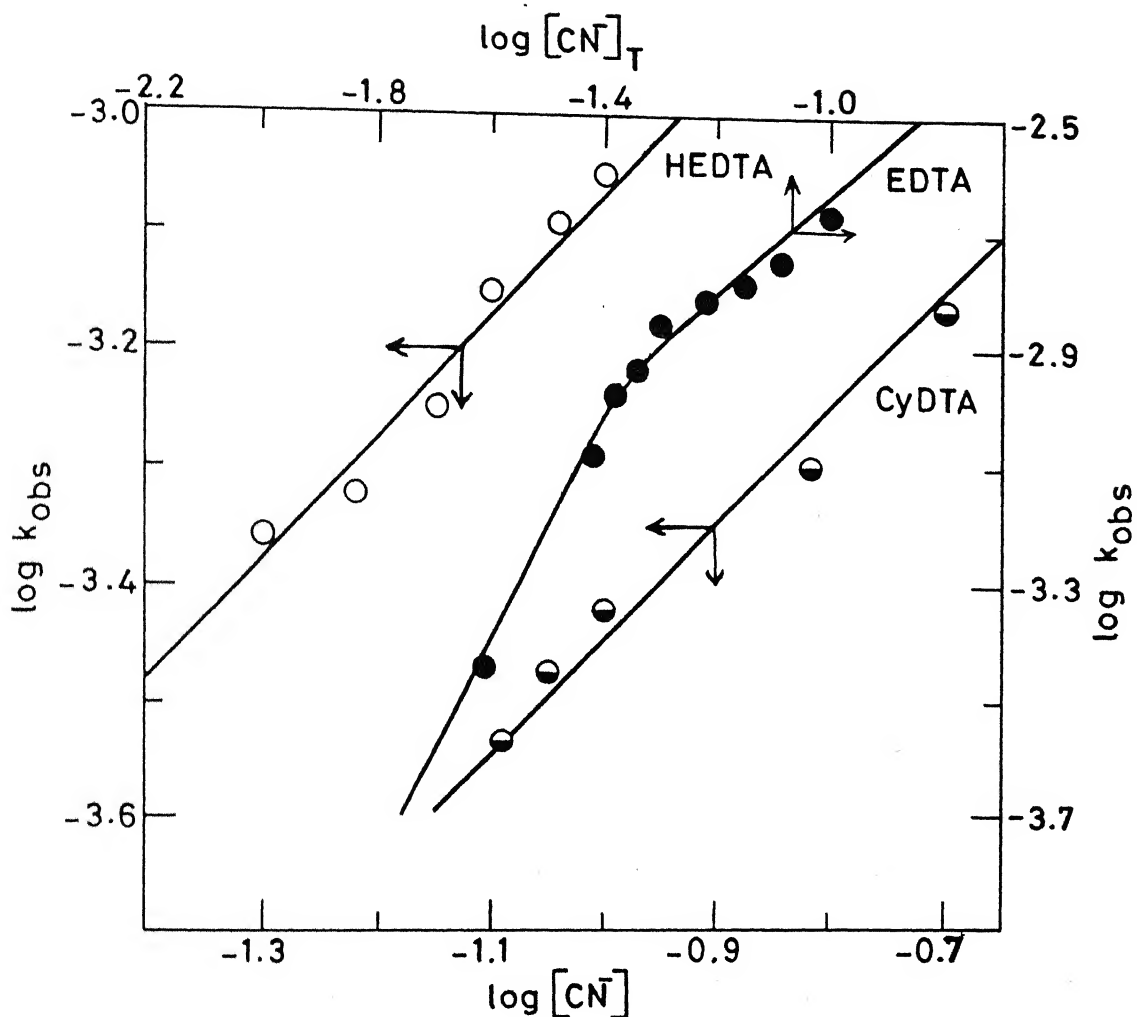


Fig.III.2 The cyanide dependence of observed pseudo-first-order rate constants for $[\text{MnL}(\text{OH})]^{2-n}-\text{CN}^-$ reaction.

The conditions are given in Table III.3.

$$\begin{aligned}
 \text{Forward rate} &= k_f [\text{MnL}(\text{CN})_x]^{3-n-x} [\text{CN}^-]^{5-x} \\
 &= k_{\text{obs}} [\text{MnL}(\text{CN})_x]^{3-n-x}
 \end{aligned} \tag{3}$$

where $k_{\text{obs}} = k_f [\text{CN}^-]^{5-x}$, $x = 4$ for CYDTA and HEDTA systems and $x = 4$ or 3 for the EDTA system.

III.5.1 pH dependence

The reaction rates of all the three systems have been studied in the pH ranges 8.5-11.0, 8.0-9.75 and 8.5-10.5 for CYDTA, HEDTA and EDTA respectively. The forward rates are found to increase with increase in pH (Fig. III.3). This increase may be due to conversion of $[\text{MnL}(\text{OH}_2)]^{3-n}$ complexes to their respective hydroxospecies and/or due to the conversion of HCN to CN^- . In the higher pH range the rates are found to level off. This is because the dominant forms of the reactants, at high pH, are $[\text{MnL}(\text{OH})]^{2-n}$ and the cyanide ion. The dependence of pseudo-first-order rate constants on pH for all the three systems are compiled in Table III.4.

The changes in rate with increase in pH in the stated ranges, for $\text{L}^{n-} = \text{CYDTA}^{4-}$, HEDTA^{3-} and EDTA^{4-} respectively, make it possible to resolve the rates due to $[\text{MnL}(\text{OH})]^{2-n}$ species on the one hand and HCN and CN^- on the other. The resolution of rate constants has been done by the following procedure.

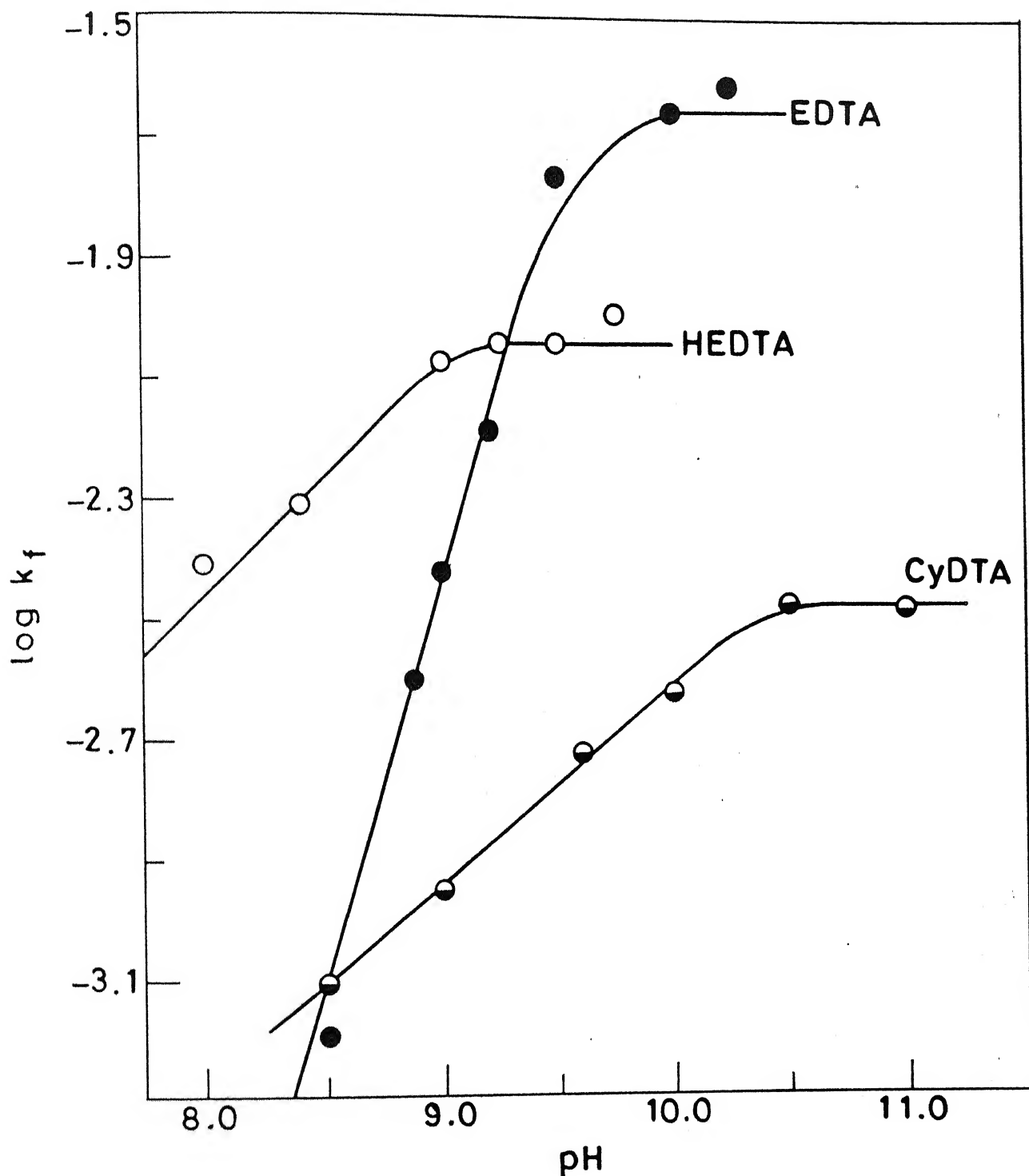


Fig.III.3 Effect of pH on the forward reaction of cyanide ion with $[\text{MnL}(\text{OH})]^{2-n}$ complexes. Reaction conditions are given in Table III.4.

Table III.4. Effect of pH on Hexacyanomanganate(III) formation from the reaction of aminopolycarboxylatomanganate(III) with cyanide ions.

A. $[\text{MnCYDTA}(\text{OH})^{2-}] = 1.5 \times 10^{-4} \text{ M}$, $[\text{CN}^-] = 2.0 \times 10^{-1} \text{ M}$ and $I = 0.25 \text{ M} (\text{NaClO}_4)$

pH	$k_{\text{obs}}, \text{ s}^{-1}$	$k_f = k_{\text{obs}}/[\text{CN}^-], \text{ M}^{-1} \text{ s}^{-1}$
8.5	1.57×10^{-4}	7.84×10^{-4}
9.0	1.56×10^{-4}	7.84×10^{-4}
9.6	3.86×10^{-4}	1.92×10^{-3}
10.0	4.80×10^{-4}	2.40×10^{-3}
10.5	6.82×10^{-4}	3.41×10^{-3}
11.0	6.98×10^{-4}	3.49×10^{-3}

B. $[\text{MnHEDTA}(\text{OH})^{1-}] = 2.0 \times 10^{-4} \text{ M}$, $[\text{CN}^-] = 9 \times 10^{-2} \text{ M}$ and $I = 0.1 \text{ M} (\text{NaClO}_4)$

8.0	3.49×10^{-4}	3.88×10^{-3}
8.4	4.36×10^{-4}	4.85×10^{-3}
8.6	6.31×10^{-4}	7.01×10^{-3}
9.0	7.68×10^{-4}	8.53×10^{-3}
9.25	8.27×10^{-4}	9.19×10^{-3}
9.5	8.15×10^{-4}	9.11×10^{-3}
9.75	9.14×10^{-4}	1.02×10^{-2}

...contd.

Table III.4 (contd.)

C. $[\text{MnEDTA}(\text{OH})^{2-}] = 1.2 \times 10^{-3} \text{ M}$, $[\text{CN}^-] = 8.0 \times 10^{-2} \text{ M}$ and $I = 0.1 \text{ M} (\text{NaClO}_4)$

pH	$k_{\text{obs}}, \text{ s}^{-1}$	$k_{\text{f}} = k_{\text{obs}} / [\text{CN}^-], \text{ M}^{-1} \text{ s}^{-1}$
8.5	1.0×10^{-3}	1.25×10^{-2}
9.0	3.80×10^{-3}	4.75×10^{-2}
9.2	6.61×10^{-3}	8.26×10^{-2}
9.5	1.77×10^{-2}	2.21×10^{-1}
10.0	2.23×10^{-2}	2.79×10^{-1}
10.25	2.50×10^{-2}	3.13×10^{-1}

In the following expression $[\text{CN}^-]_T$ includes concentrations of both forms of cyanide (equation.4).

$$k_f[\text{CN}^-]_T = k_{f(\text{CN}^-)}[\text{CN}^-] + k_{f(\text{HCN})}[\text{HCN}] \quad (4)$$

The above equation (4) can further be transformed to equation (5) by the following step:

$$k_f([\text{CN}^-] + K_{\text{HCN}}[\text{H}^+][\text{CN}^-]) = k_{f(\text{CN}^-)}[\text{CN}^-] + k_{f(\text{HCN})}K_{\text{HCN}}[\text{H}^+][\text{CN}^-]$$

$$\text{or } k_f = (k_{f(\text{CN}^-)} + k_{f(\text{HCN})}K_{\text{HCN}}[\text{H}^+]) / (1 + K_{\text{HCN}}[\text{H}^+]) \quad (5)$$

At $\text{pH} < 9$, $K_{\text{HCN}}[\text{H}^+] \gg 1$ and equation(5) reduces to equation (6).

$$k_f = (k_{f(\text{CN}^-)} / K_{\text{HCN}}) 1/[\text{H}^+] + k_{f(\text{HCN})} \quad (6)$$

Plots of k_f versus $1/[\text{H}^+]$ are linear as predicted by equation (6) (Fig. III.4). The values of $k_{f(\text{CN}^-)}$ and $k_{f(\text{HCN})}$ are estimated from the slope and the intercept respectively. The calculated values of $k_{f(\text{CN}^-)}$ and $k_{f(\text{HCN})}$ for the three systems are given in Table III.5. In all the systems the rate due to CN^- are found to be higher than those due to HCN . This is understandable because the former is a stronger nucleophile than the latter. It is also noted that the limiting rates of k_f are higher than the resolved rates due to $[\text{CN}^-]$. This appears to be, due to the decomposition of $[\text{MnL}(\text{OH})]^{2-n}$ coupled with the formation of $[\text{Mn}(\text{CN})_6]^{3-}$ in the

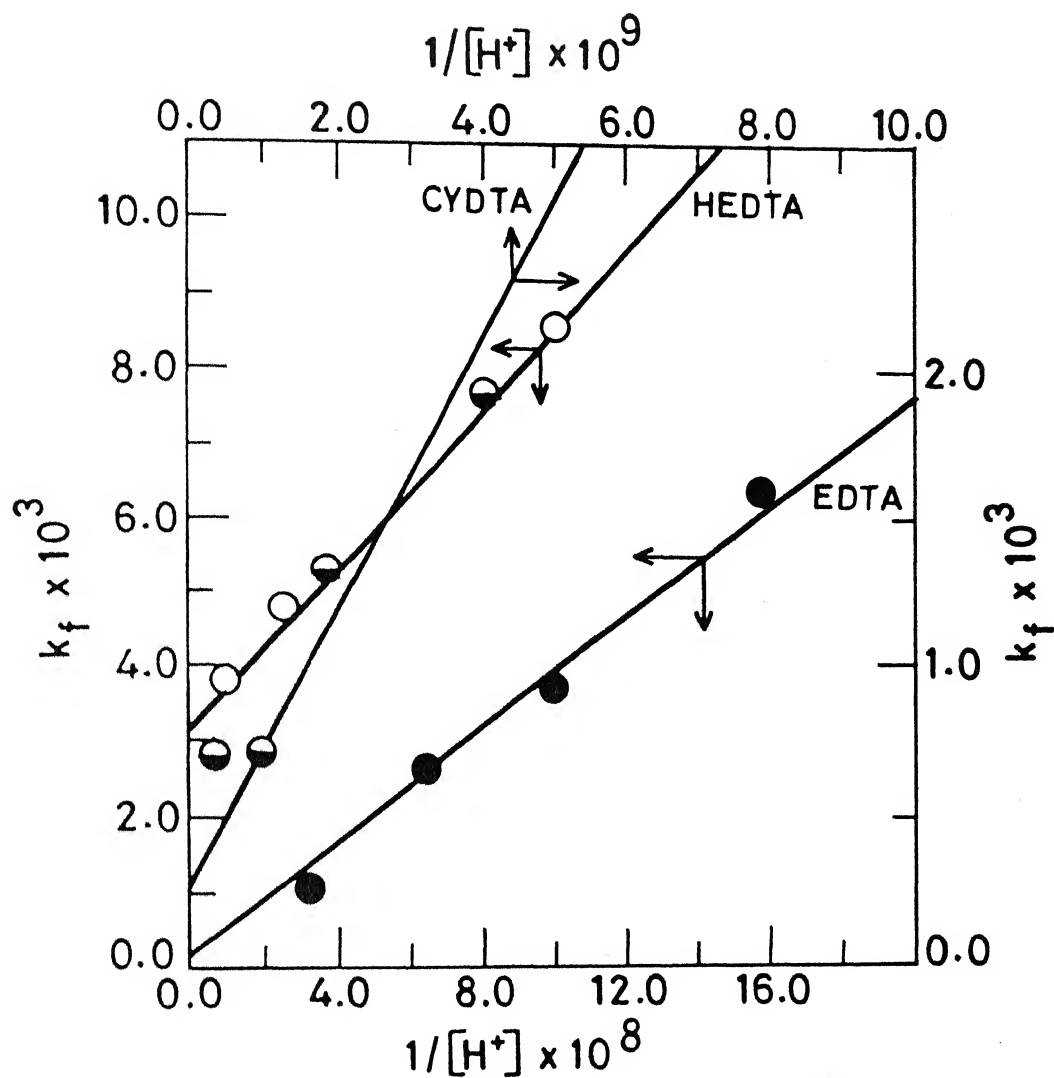


Fig.III.4 Resolution of rate constants due to CN^- and HCN for $[\text{MnL}(\text{OH})]^{2-n} - \text{CN}^-$ reaction systems.

Table III.5. Resolved rate constants: $k_{\text{[MnL(OH)]}^{\text{CN}^-}}$ and $k_{\text{[MnL(OH)]}^{\text{HCN}}}$ in the $[\text{MnL(OH)}]^{2-n} - \text{CN}^-$ reaction.

L^{n-}	$k_{\text{f(HCN)}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{f(CN}^-)}, \text{M}^{-1} \text{s}^{-1}$
CYDTA ⁴⁻	2.5×10^{-4}	6.8×10^{-4}
HEDTA ³⁻	3.2×10^{-3}	1.25×10^{-2}
* EDTA ⁴⁻	2.0×10^{-4}	6.3×10^{-3}

* Ref. 19,20.

presence of excess cyanide by this alternative path in addition to the main substitution reaction taking place in all the three systems. The decomposition of $[\text{MnL}(\text{OH})]^{2-n}$ has been reported.²⁵

III.5.2 Ionic strength dependence

The forward reaction rates are found to increase with increase in ionic strength of the medium. The ionic strengths of the reaction medium are maintained each time before mixing, keeping pH, temperature and concentrations constant during a kinetic run. The forward rate constants for the reaction of $[\text{MnL}(\text{OH})]^{2-n}$ with cyanide ion follow the Bronsted-Bjerrum equation (7).

$$\log k_f = \log k_o + 1.02 Z_A Z_B \sqrt{I} / (1 + \sqrt{I}) \quad (7)$$

where k_f is the specific rate constant, k_o is the specific rate constant at zero ionic strength, while Z_A and Z_B are charges on the two reactant species. The rate constants at different ionic strengths are listed in Table III.6. The value of $Z_A Z_B$ calculated from the slopes of these plots (Fig. III.5) agree with the expected values for the rate-determining step envisaged in the mechanistic scheme. This is an additional evidence in support of the postulate that the fifth step is the rate determining one in the six step mechanism proposed for the reaction systems (vide supra).

Table III.6. Effect of ionic strength on forward rate constants for $[\text{MnL}(\text{OH})]^{2-n} - \text{CN}^-$ reactions at 25°C . Other conditions are same as in Table III.4.

	I, M(NaClO_4)	$k_{\text{obs}}, \text{s}^{-1}$
A. CYDTA^{4-}		
	0.2	4.9×10^{-4}
	0.25	6.82×10^{-4}
	0.30	7.68×10^{-4}
	0.34	1.0×10^{-3}
B. HEDTA^{3-}		
	0.1	8.15×10^{-4}
	0.15	1.29×10^{-3}
	0.2	1.40×10^{-3}
	0.25	1.68×10^{-3}
C. EDTA^{4-}		
	0.07	9.96×10^{-4}
	0.09	1.44×10^{-3}
	0.10	2.34×10^{-2}

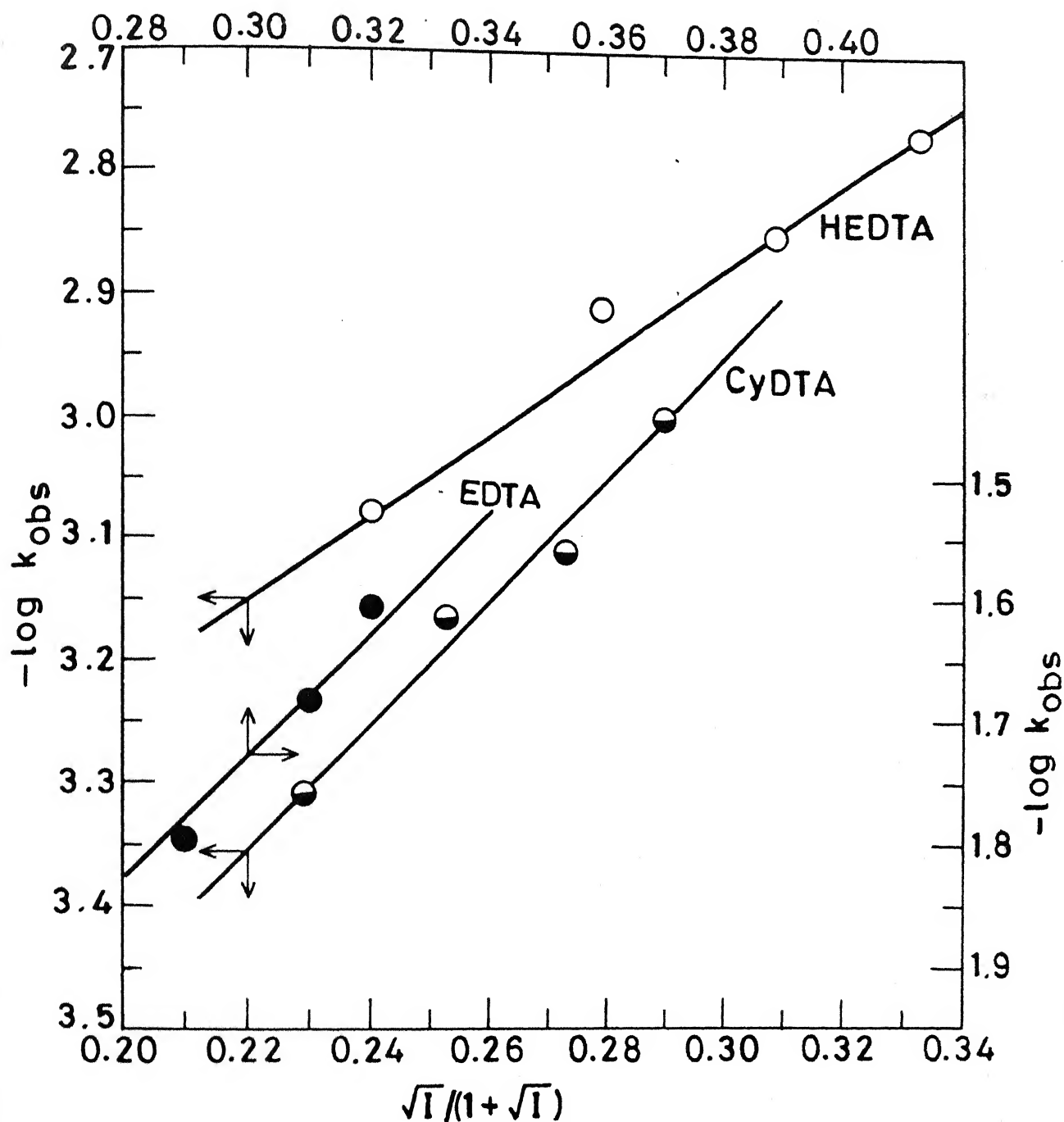


Fig.III.5 Effect of ionic strength on forward reaction rate for $[\text{MnL}(\text{OH})]^{2-n} - \text{CN}^-$ systems. Reaction conditions are specified in Table III.6.

III.6 Kinetics of Reverse Reactions

The reverse reactions i.e. the reaction between $[\text{Mn}(\text{CN})_6^{3-}]$ and L^{n-} (always present in large excess) have been carried out by adding crystals of $\text{K}_3[\text{Mn}(\text{CN})_6]$ into an alkaline solution of the ligand L^{n-} . The reverse reactions are followed from the formation of the products i.e., $[\text{MnL}(\text{OH})]^{2-n}$ and follow a general rate expression given in equation (8).

$$\begin{aligned}\text{Reverse rate} &= d[\text{MnL}(\text{OH})^{2-n}]/dt = -d[\text{Mn}(\text{CN})_6^{3-}]/dt \\ &= k_r[\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}]/[\text{CN}^-] = k'_{\text{obs}}[\text{Mn}(\text{CN})_6^{3-}]/[\text{CN}^-] \quad (8)\end{aligned}$$

where $k'_{\text{obs}} = k_r[\text{L}^{n-}]$.

An integrated rate expression for eqn. (8) can be derived in terms of the concentration of $[\text{MnL}(\text{OH})]^{2-n}$ and is given in equation (9).

$$A_{\infty} \ln \frac{A_{\infty} - A_t}{A_{\infty}} + A_t = - \epsilon \cdot l \cdot k'_{\text{obs}} \cdot t/6 \quad (9)$$

where A_{∞} represents the absorbance of the species $[\text{MnL}(\text{OH})]^{2-n}$ at infinite time, A_t at time t , l is the path length and ϵ is the molar extinction coefficient of $[\text{Mn}(\text{CN})_6^{3-}]$. The inverse-first-order plots for $[\text{Mn}(\text{CN})_6^{3-}] - \text{L}^{n-}$ reactions are shown in Fig.III.6. The rate constants for the same are compiled in Table III.7 for CYDTA, HEDTA and EDTA systems. The observed inverse-first-order

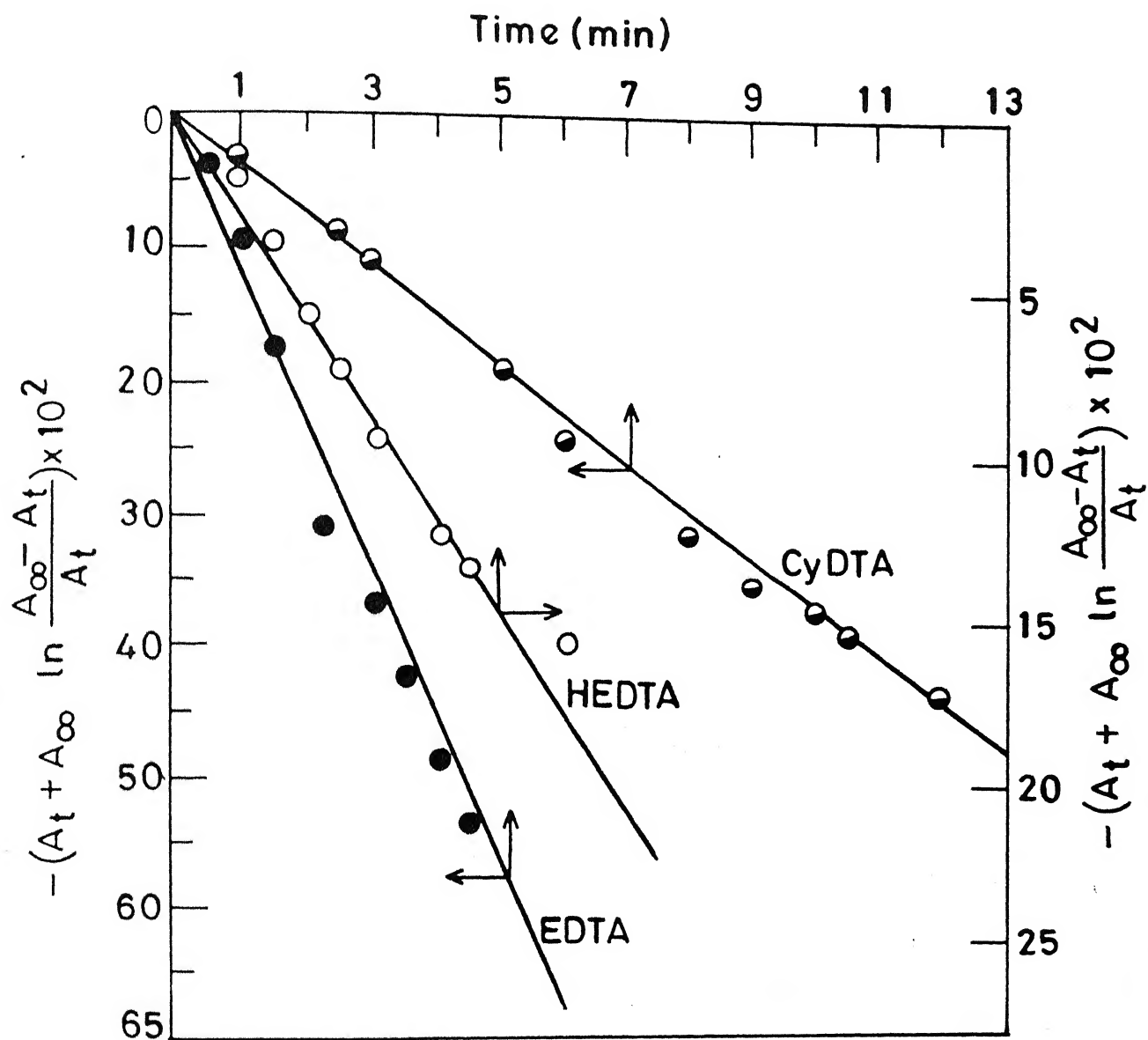


Fig. III. 6

Inverse-first-order plots for the reaction of Mn(CN)_6^{3-} with L^{n-} ; $[\text{Mn(CN)}_6^{3-}] = 5 \times 10^{-4} \text{ M}$, $[\text{CyDTA}^{4-}] = [\text{EDTA}^{4-}] = 1.5 \times 10^{-2} \text{ M}$, pH = 10 and $[\text{HEDTA}^{3-}] = 9 \times 10^{-3} \text{ M}$ and pH = 9.5.

Table III.7. Kinetics of reverse reactions

Conditions: $\text{pH} = 10.0 \pm 0.02$, $I = 0.1\text{M}(\text{NaClO}_4)$,

$[\text{Mn}(\text{CN})_6]^{3-} = 5 \times 10^{-4}\text{M}$, $\text{temp.} = 30 \pm 0.1^\circ\text{C}$.

A. $[\text{CYDTA}^{4-}]_{\text{T}}, 10^2\text{M}$	$k'_{\text{obs}}, 10^{-4}, \text{M s}^{-1}$	$k_{\text{r}} = k'_{\text{obs}} / [\text{L}^{n-}] 10^2, \text{s}^{-1}$
1.0	8.21	8.20
1.5	12.6	8.41
2.0	16.3	8.13
<hr/>		
$k_{\text{f}}(\text{av}) = (8.25 \pm 0.12) \times 10^{-2}, \text{s}^{-1}$		
B. $[\text{HEDTA}^{3-}]_{\text{T}}, 10^3\text{M}$	$k'_{\text{obs}}, 10^6, \text{M s}^{-1}$	$k_{\text{r}}, 10^4, \text{s}^{-1}$
9.0	3.49	3.88
9.5	3.62	3.88
10.0	3.82	3.82
20.0	7.76	3.81
<hr/>		
$k_{\text{r}}(\text{av}) = (3.85 \pm 0.03) \times 10^{-4}, \text{s}^{-1}$		
C. $[\text{EDTA}^{4-}]_{\text{T}}, 10^3\text{M}$	$k'_{\text{obs}}, 10^3, \text{M s}^{-1}$	$k_{\text{r}}, 10^1, \text{s}^{-1}$
6.0	1.05	1.75
7.0	1.12	1.60
8.0	1.27	1.59
10.0	1.62	1.62
<hr/>		
$k_{\text{r}}(\text{av}) = (1.64 \pm 0.06) \times 10^{-1}, \text{s}^{-1}$		

dependence in cyanide leads to the important inference that a step preceding the last step is rate-determining.

III.7 Temperature dependence of Forward and Reverse reactions

The rate constants for the forward reactions between $[\text{MnL}(\text{OH})]^{2-n}$ and cyanide ions have been determined for all the three systems (in the range of first-order dependence in $[\text{CN}^-]$) between 18-45°C and that of the reverse reactions over the range 15-35°C. Both forward and reverse rates are found to follow the Arrhenius equation (10).

$$\ln k = - E_a/RT + \ln A \quad (10)$$

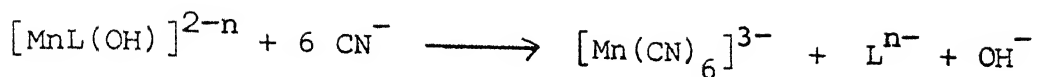
The values of entropies of activations for the forward and reverse reactions are calculated from the Eyring equation (11).

$$k_2 = \frac{k_B T}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT} \quad (11)$$

where all terms have their usual meanings. The values of the activation parameteres (ΔH^\ddagger and ΔS^\ddagger) for both forward and reverse reactions are listed in Table III.8.

Table III.8. Activation parameters

Forward reactions:



L^{n-}	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{JK}^{-1}\text{mol}^{-1}$
CYDTA ⁴⁻	47.5 ± 0.5	-285 ± 6
HEDTA ³⁻	43.4 ± 0.7	-292 ± 6
EDTA ⁴⁻	42.8 ± 0.7	-277 ± 5

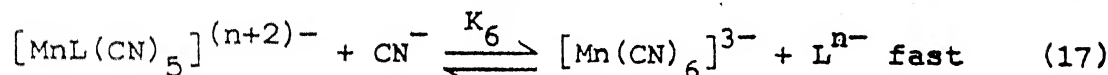
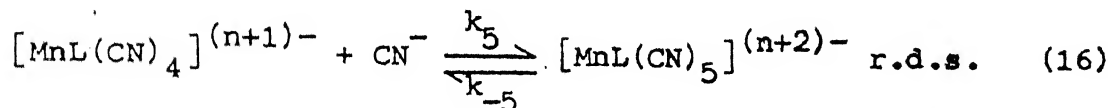
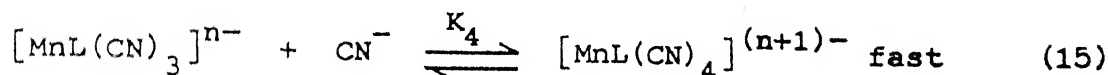
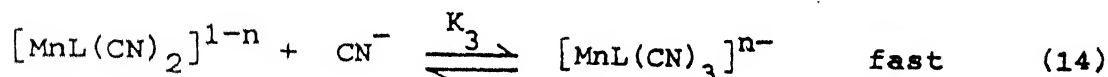
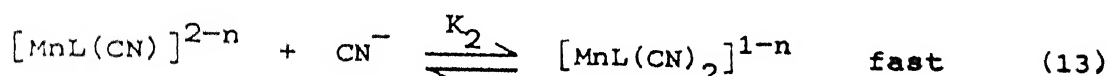
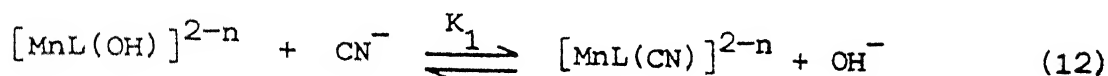
Reverse reactions:



CYDTA ⁴⁻	93.6 ± 0.6	-266 ± 3
HEDTA ³⁻	66.8 ± 0.5	-311 ± 2
EDTA ⁴⁻	92.7 ± 0.5	-259 ± 2

III.8 Discussion

Based on the experimental observations on the rates of forward and reverse reactions, a general six-step mechanism is proposed from equations (12-17).



where $\text{L}^{n-} = \text{CYDTA}^{4-}$, HEDTA^{3-} and EDTA^{4-}

A first-order dependence in $[\text{CN}^-]$ in case of CYDTA and HEDTA and a variable order dependence changing from one at high to two at low $[\text{CN}^-]$ in case of EDTA have been observed. Observance of a variable order dependence in $[\text{CN}^-]$ points to the fact that step-wise substitution of L^{n-} by the cyanide ions takes place while the ligand unwraps itself from the coordination sphere of Mn(III). Observation of higher order in $[\text{CN}^-]$ has not been possible because the reactions become too slow to be followed

experimentally at low enough $[\text{CN}^-]$ where these dependences might have been observed. A variable order dependence in case of substitution reaction on NiL^{1-11} and $\text{FeL}(\text{OH})^{12-17}$ by cyanide has been observed earlier and interpreted to lead to the above conclusion.

The rate expression for the reverse reaction can be derived by applying steady state treatment to the intermediate viz. $[\text{MnL}(\text{CN})_4]^{(n+1)-}$ produced in the rate-determining step of the postulated mechanism.

$$\begin{aligned} d[\text{MnL}(\text{CN})_5^{(n+2)-}]/dt &= k_5[\text{MnL}(\text{CN})_4^{(n+1)-}][\text{CN}^-] \\ &- k_5[\text{MnL}(\text{CN})_5^{(n+2)-}] \\ &- k_6[\text{MnL}(\text{CN})_5^{(n+2)-}][\text{CN}^-] \\ &+ k_{-6}[\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}] = 0 \end{aligned} \quad (18)$$

$$[\text{MnL}(\text{CN})_5^{(n+2)-}] = \frac{k_5[\text{MnL}(\text{CN})_4^{(n+1)-}][\text{CN}^-] + k_{-6}[\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}]}{k_{-5} + k_6[\text{CN}^-]} \quad (19)$$

In presence of excess ligand the first term in the numerator of equation (19) can be ignored. The results on the forward and reverse rate study suggest that the sixth step is a fast one compared to fifth one and, therefore, the values of k_5 and also

k_{-5} must be relatively small. Thus even though $[\text{CN}^-]$ may be small, $k_6[\text{CN}^-]$ may still be quite large compared to k_{-5} which may be ignored in the denominator. With these assumptions the above equation (19) reduces to equation (20).

$$\begin{aligned} [\text{MnL}(\text{CN})_5^{(n+2)-}] &= \frac{k_{-6}}{k_6} [\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}]/[\text{CN}^-] \\ &= K_6^{-1} [\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}]/[\text{CN}^-] \end{aligned} \quad (20)$$

where $K_6^{-1} = k_{-6}/k_6$

On substitution for concentration of $[\text{MnL}(\text{CN})_5^{(n+2)-}]$ in the rate equation for the rate-determining step of the reverse reaction, one finally ends up with equation (21).

$$\begin{aligned} \text{rate} &= d[\text{MnL}(\text{OH})^{2-n}]/dt = -d[\text{Mn}(\text{CN})_6^{3-}]/dt \\ &= k_r [\text{Mn}(\text{CN})_6^{3-}][\text{L}^{n-}]/[\text{CN}^-] \end{aligned} \quad (21)$$

$$\text{where } k_r = k_{-5} K_6^{-1} \quad (22)$$

The above equation (21) is in conformity with the observed rate law for the reverse reaction (equation.8). The observed first order dependence in cyanide concentration for forward reactions coupled with the observation on the reverse reaction leads to the proposition that the first four steps are very fast and a stable 1:1:4 intermediates viz. $[\text{MnL}(\text{CN})_4]^{1-n}$ forms instantaneously

in each case. One cyanide reacts with $[\text{MnL}(\text{CN})_4]^{(n+1)-}$ to produce $[\text{MnL}(\text{CN})_5]^{(n+2)-}$ in the rate-determining step (equation.16). The second order dependence at low $[\text{CN}^-]$ in case of EDTA reaction is also understandable because, as the concentration of cyanide decreases the reactant becomes $[\text{MnL}(\text{CN})_3]^{n-}$ which accounts for this observation. Higher order dependences in cyanide could not be observed because the reaction become too slow for dependable measurements though variable order in cyanide, order varying from three to one, have been observed in the reaction of $\text{FeL}(\text{OH})$ with cyanide.¹²⁻¹⁷

Another support to the proposed mechanism comes from the magnitudes of activation parameters. The activation enthalpies for the forward reactions in every case is considerably lower than that for the reverse reactions (Table III.8). A large decrease in entropy of activation (ΔS^\ddagger) for the forward reactions is observed for all the systems investigated, which points to an associative mechanism rather than a dissociative one and is consistent with the rate-determining step (equation 16) in the proposed mechanism.

The first order plots of $\log C_A$ versus time 't' under pseudo-first-order conditions for the forward reactions show deviations (not shown) from linearity which are positive in each case. This cannot be due to reversibility alone because in presence of excess cyanide the reverse reaction can not occur to

any appreciable extent. So it is reasonable to suppose that the observed deviations are probably due to occurrence of some other reaction(s) involving the $[\text{MnL}(\text{OH})]^{2-n}$ complexes. One such reaction is the slow dissociation of $[\text{MnL}(\text{OH})]^{2-n}$ complex during a kinetic run.

Repetitive scans of the forward reactions for all the three systems viz. CYDTA, HEDTA and EDTA, are given in Fig.III.7, Fig.III.8 and Fig.III.9 respectively. In each system, a peak appears at 325 nm, which is due to formation of $[\text{Mn}(\text{CN})_6]^{3-}$. The height of the peak increases upto 60-70% of expected theoretical value and then decreases in the later part of the reaction. The rates of formation and decomposition of $[\text{Mn}(\text{CN})_6]^{3-}$ in case of $\text{MnCYDTA}(\text{OH}) - \text{CN}^-$ reaction, are comparable, but the peak shifts in case of HEDTA and EDTA systems are quite evident. The decrease in peak height at 325 nm (in the later stage) is attributed to the slow decomposition of $[\text{Mn}(\text{CN})_6]^{3-}$ even in presence of relatively high $[\text{CN}^-]$ under the chosen conditions. The instability of $[\text{Mn}(\text{CN})_6]^{3-}$ has been reported in literature.³³ One more peak observed between 260-270 nm at the beginning of the reactions due to $[\text{MnL}(\text{OH})]^{2-n}$ species, shifts towards 230-250 nm. This shift is due to release of the particular ligand(s) L^{n-} , which have absorption bands in this vicinity. In all the three systems two isosbestic points have been observed, one around 380 nm and other

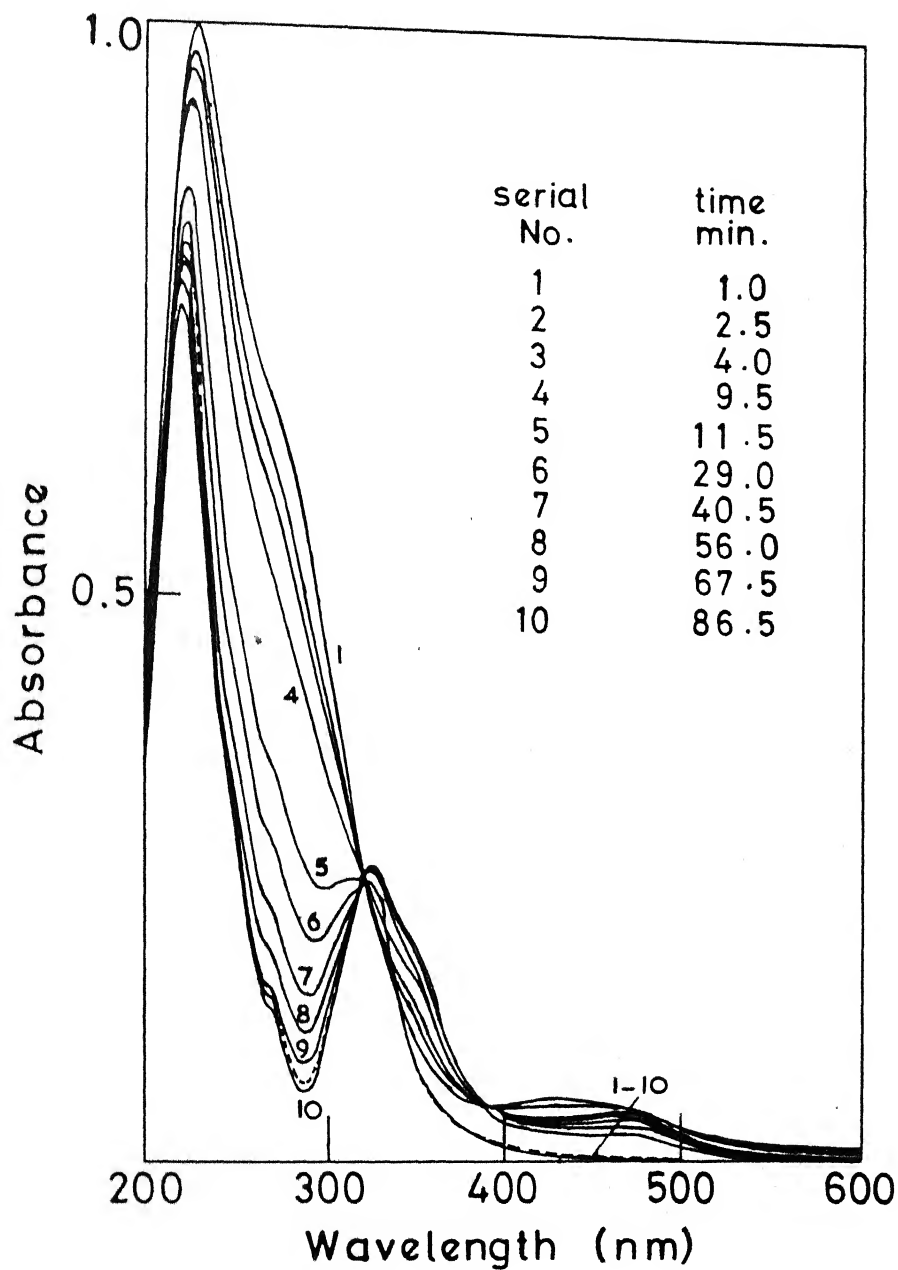


Fig.III.7 Repetitive scans of the reaction mixture during a typical kinetic run at 25°C. $[\text{Mn CyDTA}(\text{OH})^{2-}] = 10^{-4} \text{ M}$, $[\text{CN}^-] = 0.1 \text{ M}$, $\text{pH} = 10.0 \pm 0.02$ and $I = 0.1 \text{ M} . (\text{NaClO}_4)$.

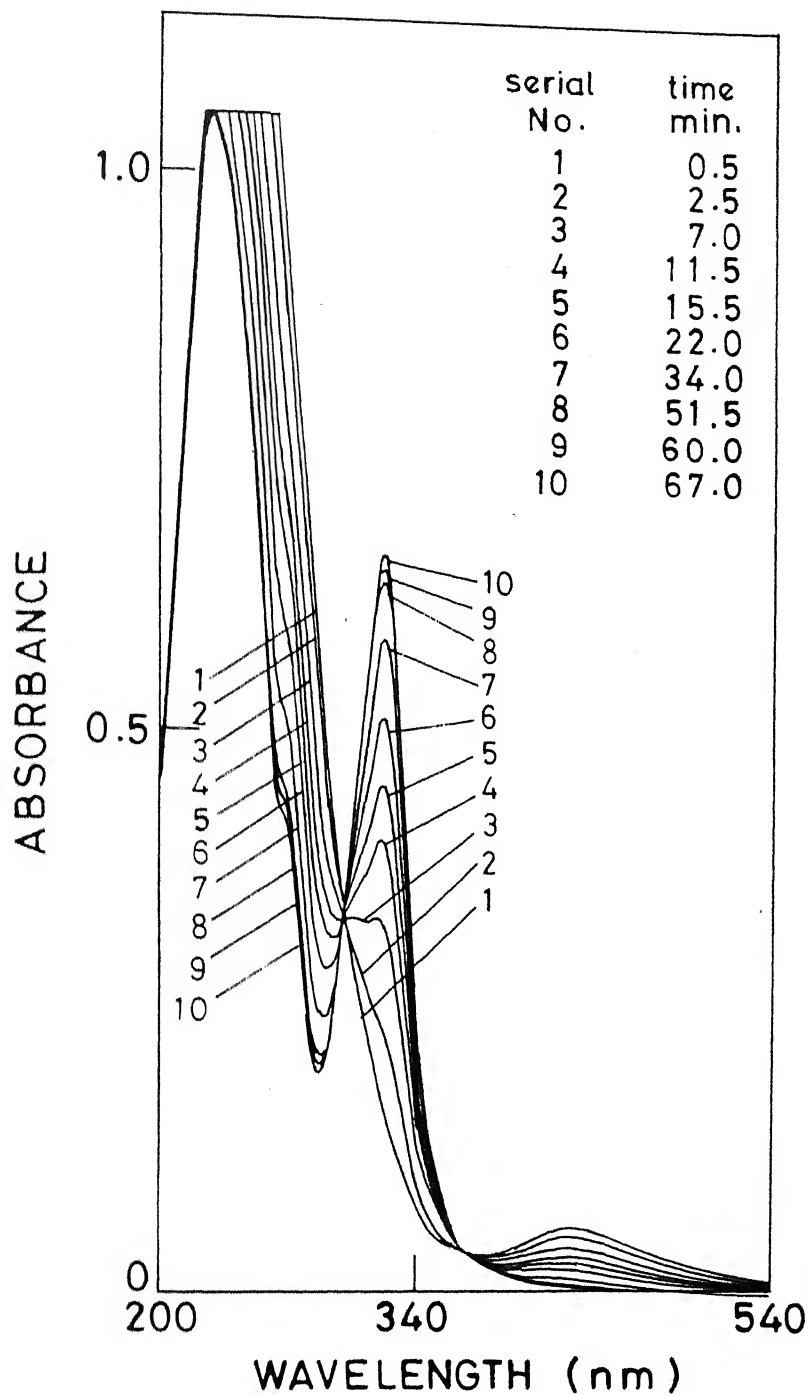


Fig.III.8 Repetitive scan of the reaction mixture during a typical kinetic run at 25°C; $[\text{MnHEDTA}(\text{OH})^-] = 1.38 \times 10^{-4} \text{ M}$; $[\text{CN}^-] = 9 \times 10^{-2} \text{ M}$, $\text{pH} = 9.5 \pm 0.02$ and $I = 0.1 \text{ M}$ (NaClO_4).

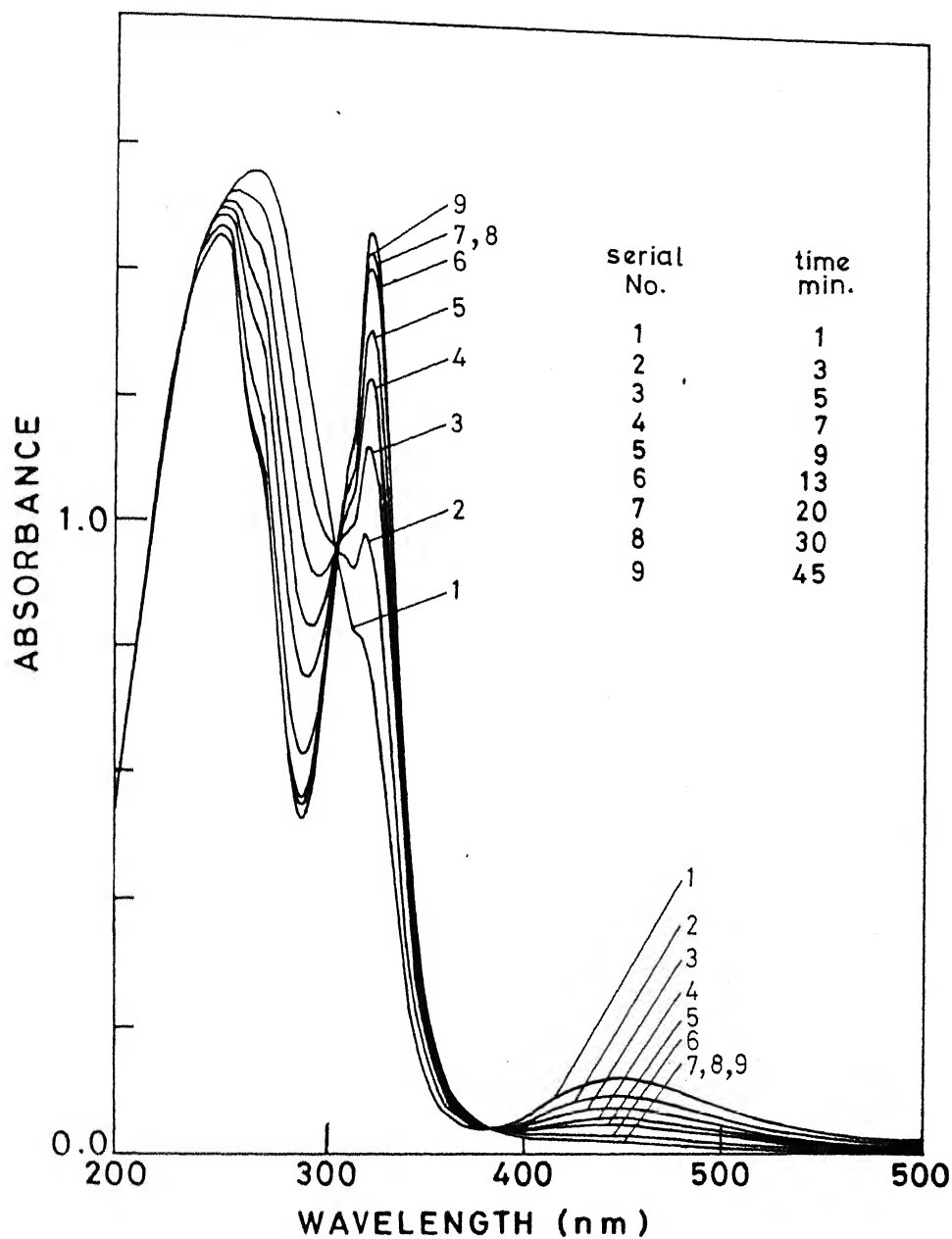
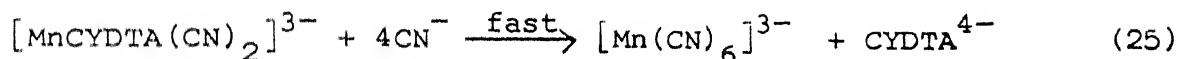
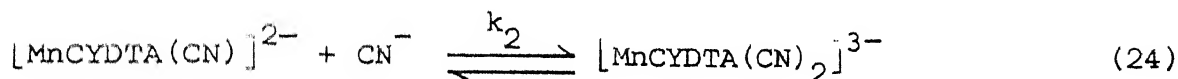
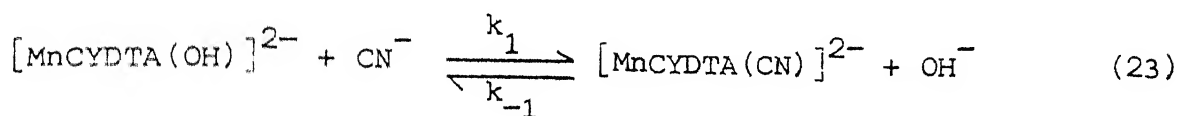


Fig.III.9 Repetitive scans of the reaction mixture during a typical kinetic run.
 $[\text{MnEDTA}(\text{OH})^{2-}] = 1.2 \times 10^{-3} \text{ M}$, $[\text{CN}^-] = 8 \times 10^{-2} \text{ M}$,
 $\text{pH} = 10.0$, $I = 0.1 \text{ M}$ and at 25°C .

around 310 nm depending on the ligands used. These are due to coexistence of $[\text{MnL}(\text{OH})]^{2-n}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ during the course of reaction.

Finally, some comment on the mechanism proposed by Hamm and Templeton¹⁸ for $\text{MnCYDTA} - \text{CN}^-$ reaction, referred to in the introduction, will be in order. Their mechanism is given below.



Their forward data plotted as $\log k_{\text{obs}}$ versus $\log [\text{CN}^-]$ exhibit a first order dependence in cyanide which is in agreement with the results obtained by us. But these workers did not investigate the reverse rate, which could provide valuable clues for identifying the rate-determining step.

With only forward rate data at their disposal, they could not possibly propose the plausible mechanism suggested by us. The observed second and first order dependences in $[\text{CN}^-]$ is not an outcome of a two step process leading to the rate-determining step (equation 25) as proposed by them. On the other hand, these dependences are logical consequences of the reactions of mixed

ligand complex intermediates $[\text{MnL}(\text{OH})(\text{CN})_3]$ and $[\text{MnL}(\text{OH})(\text{CN})_4]$ with the cyanide ions leading to the rate-determining step (equation 15) in a six step sequence.

At the risk of repetition it is stated that the effects of temperature and ionic strength lend additional support to the mechanism proposed by us. Further it may be reemphasised that this mechanism may prove general for this class of reactions.

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CHAPTER IV

STUDY ON KINETICS AND MECHANISM OF LIGAND SUBSTITUTION REACTIONS OF AMINOCARBOXYLATOPALLADATE(II) COMPLEXES WITH CYANIDE IONS BY STOPPED FLOW TECHNIQUE

ABSTRACT

Kinetics and mechanism of the reactions of $[\text{PdL}(\text{OH})_x]^{2-n-x}$ with cyanide ions have been studied by stopped flow technique ($\text{L}^{n-} = \text{EDTA}^{4-}$, Ethylenediaminetetraacetate anion and IDA^{2-} , Iminodiacetate anion). The reactions between $[\text{PdEDTA}(\text{OH})]^{3-}$ or $[\text{PdIDA}]$ with cyanide ions are studied under pseudo-first-order conditions at 350 nm (λ_{max} of $\text{PdEDTA}(\text{OH})$) and at 330 nm (λ_{max} of PdIDA), pH = 11.5 and 11.0 respectively for the two systems. The other conditions are $I = 0.1\text{M}(\text{NaClO}_4)$ and temp. = $25 \pm 0.1^\circ\text{C}$.

The forward reaction of $\text{PdEDTA}(\text{OH})-\text{CN}^-$ system shows a variable order dependence in cyanide ions, and the order changes from one at high cyanide concentration to zero at low cyanide concentration. On the other hand, only a first order dependence in cyanide ions is seen in case of PdIDA . Both the reaction systems are found to exhibit a first order dependence with respect

to the corresponding metal complexes. The reverse reaction is thermodynamically unfavourable and has not been observed in spite of repeated efforts even in presence of large excess of ligands.

IV.2 Introduction

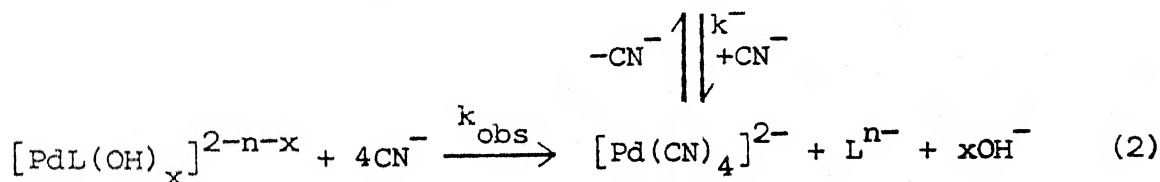
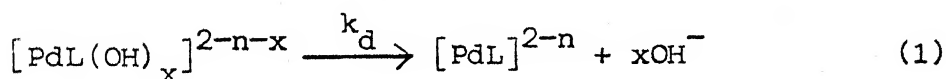
Among the substitution reactions of square planar complexes those of platinum(II) have received maximum attention.¹⁻³ A brief survey of literature on ligand substitution reactions of Pd(II) has been given in chapter I.1. Some relevant examples are also cited here.⁴⁻⁶ The kinetics of fast substitution reactions of square planar complexes had to await the discovery of techniques like stopped flow, pressure-jump and temperature-jump. The square planar substitution reactions have been investigated to a much lesser extent than the octahedral complexes.

An excellent review has been attempted on reactions between aminopolycarboxylatonickelate(II) complexes with cyanide ions.⁷ Reactions of square planar complexes of Ni(II) with cyanide ions has been carried out by Billo.⁸ Hynes and Brannick⁹ have investigated the kinetics and mechanism of the reaction between dithiocarbamate complexes of Pd(II) and cyanide ions. After a long lapse, ligand substitution reactions of Pd(II), complexed to both monodentate and multidentate ligands, have been studied in our laboratory. An investigation of the kinetics and mechanism

of reactions of PdPAR(OH) (Par = 4-(2-pyridylazo)resorcinol) with cyanide ions has been carried out recently¹⁰ using stopped flow technique and a four step mechanism has been proposed for the same. Kinetics and mechanism of the reactions of PdIDA with EDTA and TTHA have been investigated and a two step mechanism has been proposed.¹¹

The subject matter of this chapter is the description and interpretation of the results of the substitution of aminocarboxylates complexed to Pd(II) by the monodentate cyanide ions in our pursuit for better understanding of square planar substitution processes.

The $[\text{PdL}(\text{OH})_x]^{2-n-x} - \text{CN}^-$ reaction system, can be represented by equations (1) and (2).



where $\text{L}^{n-} = \text{EDTA}^{4-}$ and IDA^{2-} ; $x = 1$ and 0 for EDTA and IDA respectively and k_{obs} 's are the experimental rate constants for the forward reaction in each case. $[\text{Pd}(\text{CN})_4]^{2-}$ is the end product in both the cases. However, reaction (1) does not take place in case of PdIDA-CN⁻ system because the hydroxy group is nonexistent in the complex itself.

IV.3 Experimental

Unless stated otherwise, reagents of AR (BDH) grade have been used. The stock solution of $[\text{PdCl}_4]^{2-}$ is prepared by a literature method¹² and standardised gravimetrically using dimethylglyoxime.¹³ The mono complexes of Pd(II) are prepared by mixing solutions containing stoichiometric amounts of $[\text{PdCl}_4]^{2-}$ with recrystallized disodium salt of ethylenediaminetetraacetate or iminodiacetate anion. Tetracyanopalladate(II) is prepared by taking palladous chloride and potassium cyanide in stoichiometric amounts as the starting materials.¹⁴ Sodium cyanide (May and Baker, England) is standardized argentometrically.¹⁵ HClO_4 (E. Merck) or NaOH is used to maintain the pH at any desired value. NaClO_4 is used for maintaining ionic strength.

A stopped flow spectrophotometer model SF-3A from Hi-tech (England) equipped with a storage oscilloscope model OS-768S (ECIL, INDIA) and model DSS 6521 digital storage oscilloscope (Kekushi Corporation, Japan) are used for the study. A polaroid camera is used to record the kinetic traces. A digital pH meter model LI-120 (Elico, India) is used for all pH measurements, BDH buffers are used for standardization of pH meter. A Shimadzu double beam spectrophotometer model UV-240, with a circulatory arrangement for thermostating the cell compartment, and an ultracryostat model 2 NBE (VEB Kombinat Medizin and Labortechnik Kombinatbetriebe, GDR) are

used to maintain the temperature of the reactants. Triple distilled water is used for the preparation of the complexes and rinsing of glass ware.

IV.4 Results

IV.4.1 Kinetic Measurements

Pd(II) forms mononuclear 1:1 complexes with EDTA⁴⁻¹² and IDA²⁻¹⁶ in the chosen experimental conditions. The names and structures of the aminopolycarboxylates are given in Table IV.1. The protonation constants of the ligands and stability constants of the metal complexes concerned, are given in Table IV.2. The absorption spectra of PdEDTA(OH) and PdIDA are given in Fig. IV.1. The species involved in the reaction conditions are $[PdL(OH)_x]^{2-n-x}$ on the one hand whereas cyanide (existing mainly as CN^-) on the other.

The reaction between $[PdL(OH)_x]^{2-n-x}$ and cyanide ions has been followed spectrophotometrically at $\lambda = 350$ nm and 330 nm by stopped flow techniques. The reaction conditions are: pH = 11.5 \pm 0.02 for EDTA, and pH = 11.0 \pm 0.02 for IDA systems. The other conditions are I = 0.1M ($NaClO_4$) and temp. = 25°C. A spectral scan of PdEDTA(OH)- CN^- system is shown in Fig. IV.2. Oscillograms show simple kinetic traces for PdIDA- CN^- reactions (Fig. IV.3) taken with the help of a 6521 digital storage oscilloscope coupled

Table IV.1. Names and structures of the aminocarboxylates.

L^{n-}	Name	Structure
EDTA ⁴⁻	Ethylenediamine-tetraacetate ion	$ \begin{array}{c} ^-OOCCH_2C \\ \quad \quad \quad \diagup \\ \quad \quad \quad N \cdot CH_2 \cdot CH_2 \cdot N \\ \quad \quad \quad \diagdown \\ ^-OOCCH_2C \end{array} \begin{array}{c} CH_2COO^- \\ \diagdown \\ CH_2COO^- \end{array} $
IDA ²⁻	Iminodiacetate anion	$ \begin{array}{c} CH_2COO^- \\ \diagdown \\ HN \\ \diagup \\ CH_2COO^- \end{array} $

Table IV.2. A. Protonation constants ($\log K_H$) of the aminocarboxylates.

L^{n-}	HL	H_2L	H_3L	H_4L	Ref.
EDTA ⁴⁻	10.34	6.24	2.75	2.07	17
IDA ²⁻	9.34	2.61	1.82	-	18

B. Stability constants ($\log K$) of the aminocarboxylato-palladate(II) complexes at 25°C and $I=0.1M(NaClO_4)$.

L^{n-}	PdL	PdHL	PdH ₂ L	Ref.
EDTA ⁴⁻	18.5 ^b	3.1 ^a	0.9 ^a	12
IDA ²⁻	9.62 ^a	0.75		16

^a $I = 1.0M$ and temp. = 20°C.

^b $I = 0.2M$.

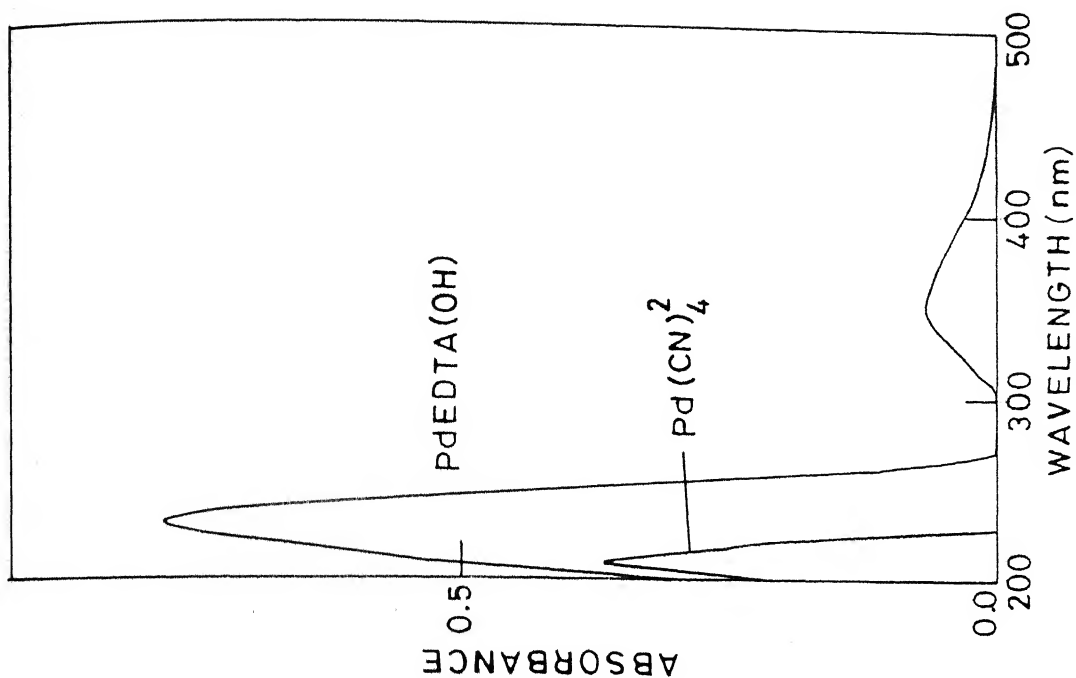


Fig.IV.2 Spectral scan of PdEDTA-(OH)-CN⁻ system.

(OH)-CN⁻ system.
 $[\text{PdEDTA(OH)}] = 1.2 \times 10^{-4} \text{ M}$,
 $[\text{CN}^-] = 2 \times 10^{-2} \text{ M}$ and $\text{pH} = 11.5$.

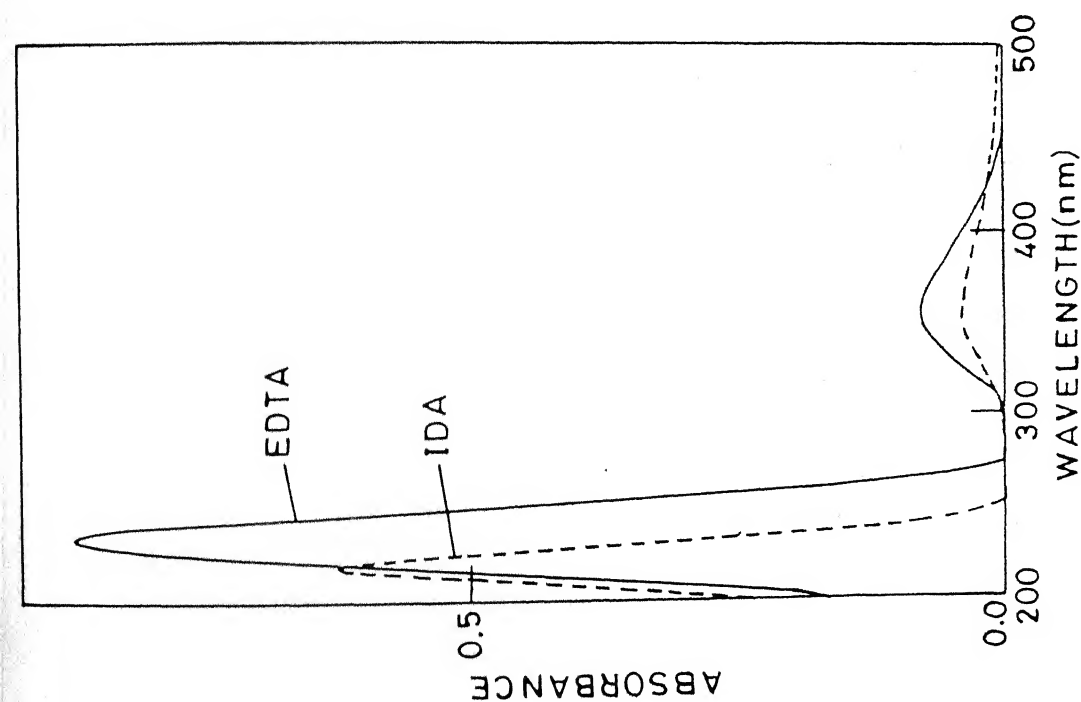


Fig.IV.1 The absorption spectra of PdIDA and PdEDTA(OH),

PdIDA and PdEDTA(OH),
 $[\text{PdIDA}] = [\text{PdEDTA(OH)}] =$
 $1.2 \times 10^{-4} \text{ M}$ and $\text{pH} = 11.5$.

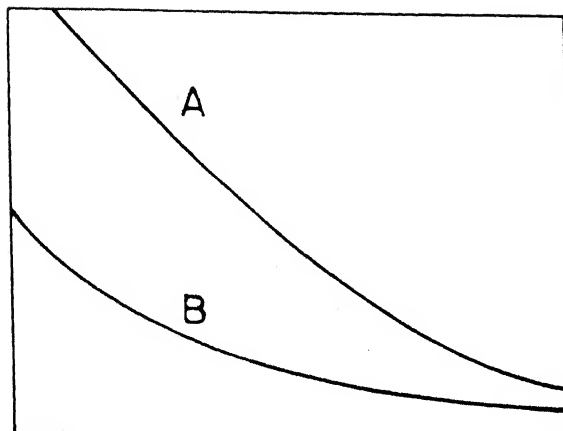


Fig.IV.3 Kinetic traces of reactions between PdIDA and cyanide ions at pH=11.5(A) and pH=11.0(B). Other conditions are as given in Table IV.4

to the stopped flow apparatus. In case of PdEDTA-CN⁻ systems also, similar traces are obtained (not shown). In both cases, pseudo-first-order plots are obtained.

IV.4 Reaction of [PdL(OH)_x]^{2-n-x} with cyanide

The rate of formation of tetracyanopalladate(II) ion are found to be first order in PdEDTA(OH) and PdIDA and show a variable order dependence in cyanide concentration in case of EDTA systems where the order in cyanide varies from one to zero at high and low cyanide concentration respectively. However, the observed order is only one for the IDA system. The zero order dependence in cyanide concentration in case of PdEDTA(OH) complex indicates a slow release of the hydroxyl ions from [PdEDTA(OH)³⁻] complex (equation.1) followed by the reaction of [PdEDTA]²⁻ with cyanide to give Pd(CN)₄²⁻ (equation 2). In case of IDA complex reaction presented by equation (1) does not occur. Thus the k_{obs} can be expressed by equation (3).

$$k_{obs} = k_d^{PdEDTA(OH)} + k'[CN^-] \quad (3)$$

where k_d and k' are found to be $0.33 \times 10^{-1} s^{-1}$ and $1.88 \times 10^2 M^{-1} s^{-1}$ respectively. The various pseudo-first-order rates constants are given in Table IV.3. A plot of $\log k_{obs}$ versus $\log [CN^-]_T$ (Fig. IV.4) shows the effect of cyanide concentration on the reaction rate.

Table IV.3. Effect of cyanide concentration on the forward rate constants at 25°C.

- A. $[\text{PdEDTA}(\text{OH})^{3-}] = (5.0 - 8.0) \times 10^{-5} \text{ M}$,
 $\text{pH} = 11.5 \pm 0.02$ and $\text{I} = 0.1 \text{ M}(\text{NaClO}_4)$.
- B. $[\text{PdIDA}] = (4.0 - 8.0) \times 10^{-5} \text{ M}$, $\text{pH} = 11.0 \pm 0.02$
and $\text{I} = 0.1 \text{ M}(\text{NaClO}_4)$.

$[\text{CN}^-]_{\text{T}}, \text{ M}$	A. $[\text{PdEDTA}(\text{OH})] - \text{CN}^-$	B. $[\text{PdIDA}] - \text{CN}^-$
	$k_{\text{obs}}, \text{ s}^{-1}$	$k_{\text{obs}}, \text{ s}^{-1}$
1.0×10^{-3}	3.38*	
2.5×10^{-3}	3.38*	
3.0×10^{-3}	-	3.01
4.0×10^{-3}	3.38*	
5.0×10^{-3}	-	3.89
6.0×10^{-3}	4.38	-
7.5×10^{-3}	4.84	5.27
9.5×10^{-3}	5.76	6.40
1.5×10^{-2}	5.92	6.62

*Zero order in cyanide.

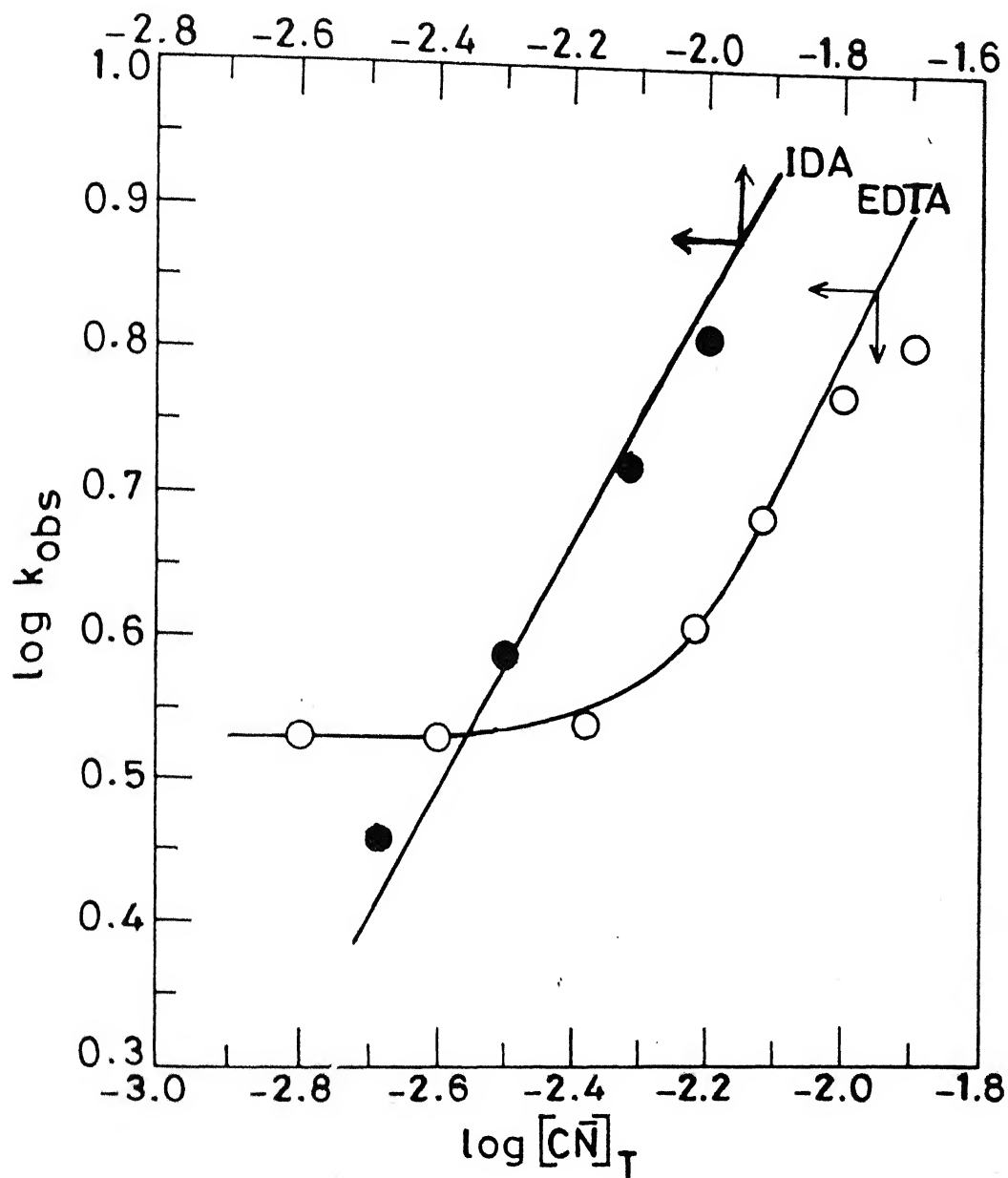


Fig.IV.4 Effect of cyanide concentration on the forward rate constants. Conditions are given in Table IV.3.

IV.4.2.1 Dependence of pH on forward reaction rates

Both the reactions have been studied over the pH range 9.0-12.0 and in the concentration range where order in $[\text{CN}^-]$ is one. The rate constants are found to increase with decrease in hydrogen ion concentration and then level off at higher pH (Fig. IV.5). This behaviour is due to different reactivities of the unprotonated and protonated forms of cyanide with the reactants. The dependences on pH is given in Table IV.4 for both the systems. Species distributions of unprotonated and protonated form of PdIDA complexes as a function of pH is shown in Fig. IV.6. The resolution of rates due to HCN and CN^- with PdIDA has been done in the pH range 9.5-11.0 where palladium complex exists mainly as PdIDA. The procedure for the same is outlined below.

$$\text{Rate} = k_f[\text{PdL}][\text{CN}^-]_T \quad (4)$$

$$\begin{aligned} \text{or Rate} &= (k_{\text{CN}}^{\text{PdL}} [\text{CN}^-] + k_{\text{HCN}}^{\text{PdL}} [\text{HCN}]) [\text{PdL}] \\ &= (k_{\text{CN}}^{\text{PdL}} [\text{CN}^-] + k_{\text{HCN}}^{\text{PdL}} K_{\text{HCN}} [\text{H}^+][\text{CN}^-]) [\text{PdL}] \\ &= (k_{\text{CN}}^{\text{PdL}} + k_{\text{HCN}}^{\text{PdL}} K_{\text{HCN}} [\text{H}^+]) [\text{PdL}][\text{CN}^-] \end{aligned} \quad (5)$$

Comparing eqn. (4) and eqn. (5), eqn. (6) is obtained

$$k_f([\text{CN}^-]_T/[\text{CN}^-]) = k_{\text{CN}}^{\text{PdL}} + k_{\text{HCN}}^{\text{PdL}} K_{\text{HCN}} [\text{H}^+] \quad (6)$$

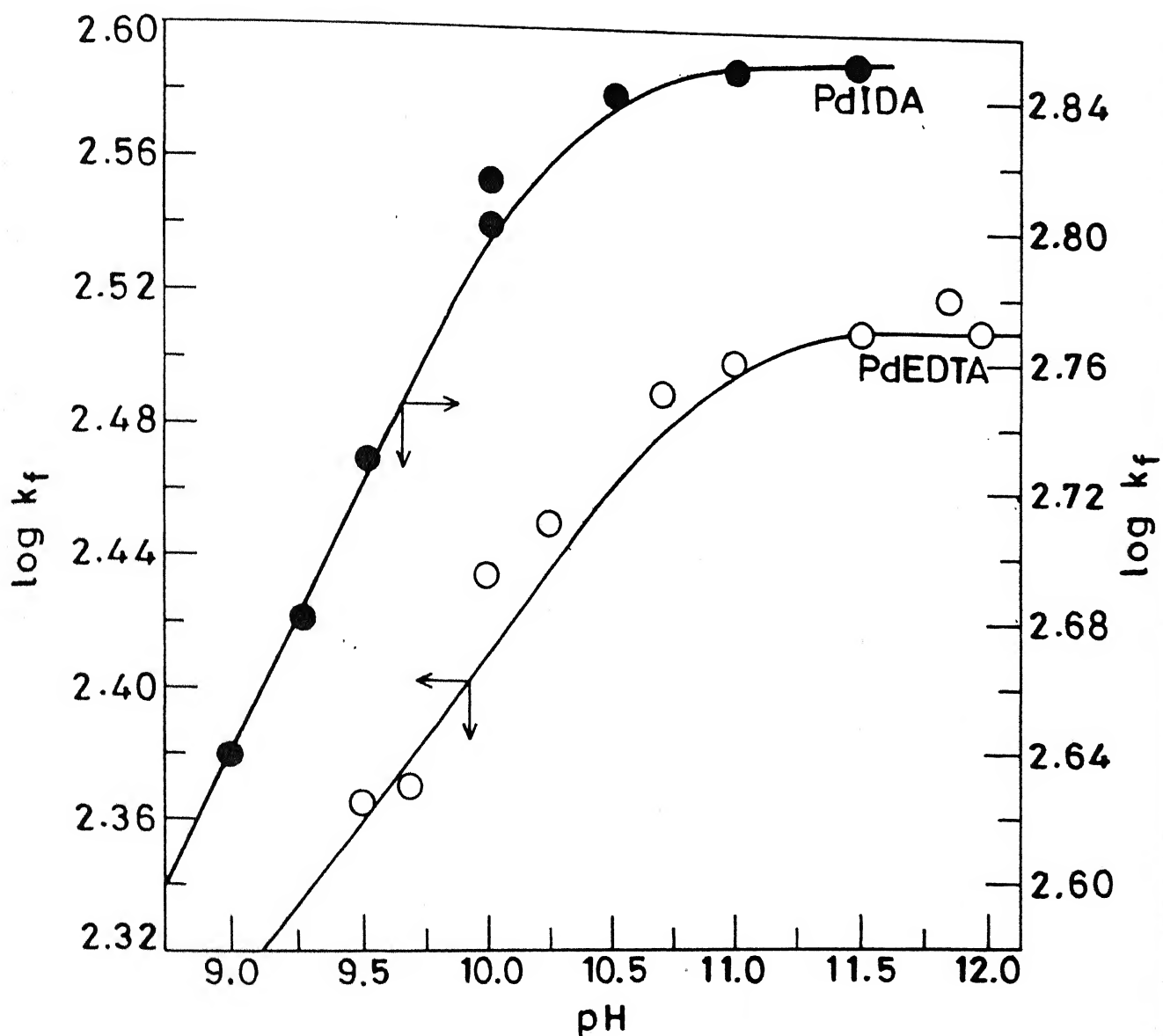


Fig. IV.5 Effect of pH on the rate constants of $\text{PdL}(\text{OH})_x^{2-n-x} - \text{CN}^-$ reactions. Conditions are given in Table IV.4.

Table IV.4. Effect of pH on the rate constants of $[\text{PdL}(\text{OH})_x]^{2-n-x} - \text{CN}^-$ reaction at 25°C and $I = 0.1\text{M}(\text{NaClO}_4)$.

A. $[\text{PdEDTA}(\text{OH})^{3-}] = 8.0 \times 10^{-5}$, $[\text{CN}^-] = 1.5 \times 10^{-2}\text{M}$

B. $[\text{PdIDA}] = 8.0 \times 10^{-5}$, $[\text{CN}^-] = 7.5 \times 10^{-3}\text{M}$

A.	pH	$k_{\text{obs}}, \text{s}^{-1}$	$k_f, 10^{-2}, \text{M}^{-1}\text{s}^{-1}$
	9.5	3.48	2.32
	9.7	3.51	2.34
	10.0	4.15	2.77
	10.25	4.27	2.85
	10.7	4.61	3.07
	11.0	4.79	3.19
	11.5	4.75	3.14
	11.85	4.94	3.29

B.	pH	$k_{\text{obs}}, \text{s}^{-1}$	$k_f, 10^{-2}, \text{M}^{-1}\text{s}^{-1}$
	9.0	3.95	4.33
	9.5	3.99	5.32
	10.0	4.89	6.52
	10.6	5.18	6.91
	11.0	5.26	7.01
	11.5	5.29	7.01

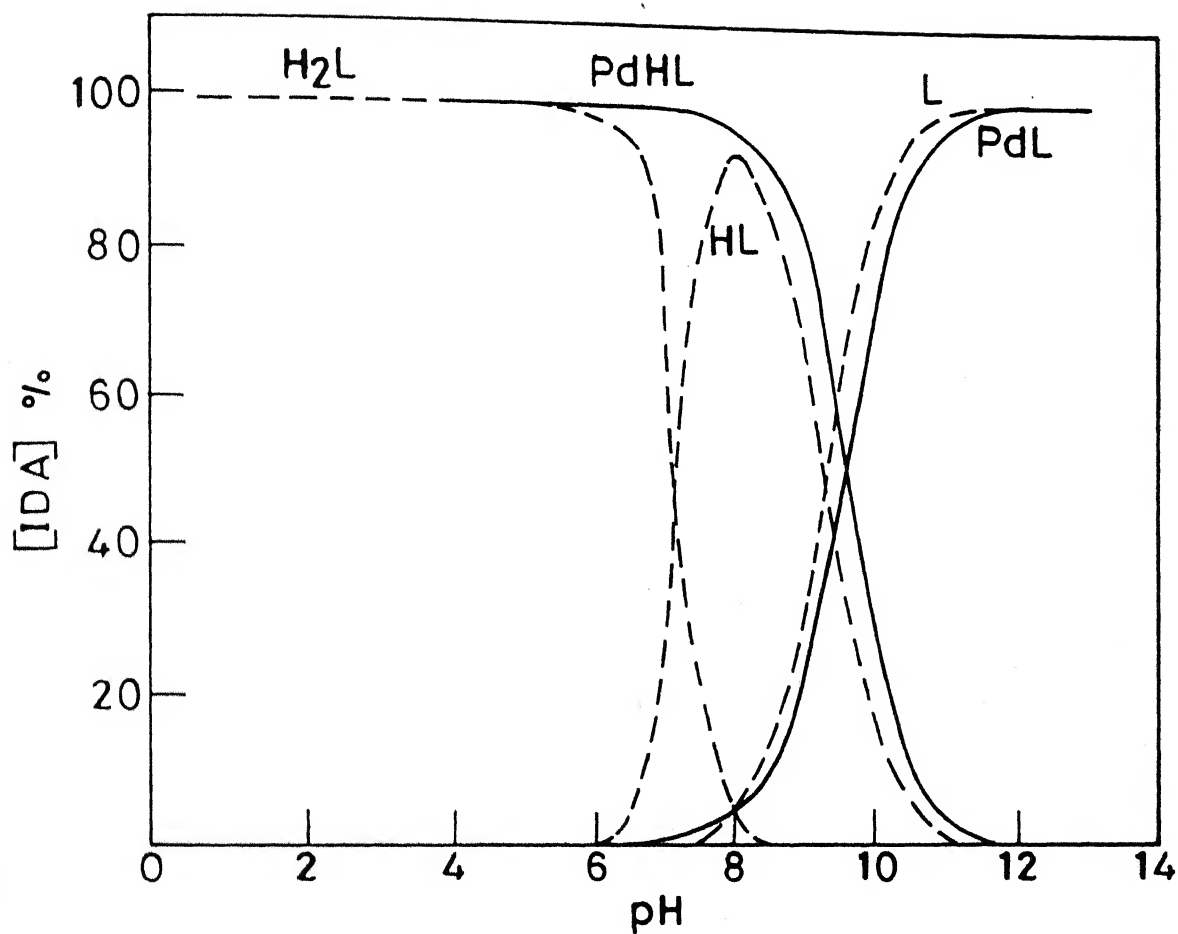


Fig.IV.6 Species distribution of IDA and PdIDA as a function of pH; $[IDA] = [Pd^{2+}] = 2.5 \times 10^{-4} M$.

Total cyanide concentration can be written in terms of its protonated and unprotonated forms as:

$$[\text{CN}^-]_T = [\text{CN}^-] + [\text{HCN}] = [\text{CN}^-](1 + K_{\text{HCN}}[\text{H}^+]) \quad (7)$$

$$\text{or } [\text{CN}^-]_T / [\text{CN}^-] = 1 + K_{\text{HCN}}[\text{H}^+] \quad (8)$$

putting equation (8) in equation (6), equation (9) is obtained.

$$k_f(1 + K_{\text{HCN}}[\text{H}^+]) = k_{\text{CN}}^{\text{PdL}} + k_{\text{HCN}}^{\text{PdL}} K_{\text{HCN}} [\text{H}^+] \quad (9)$$

By plotting LHS of eqn.(9) vs. $[\text{H}^+]$ (Fig.IV.7) $k_{\text{CN}}^{\text{PdL}}$ and $k_{\text{HCN}}^{\text{PdL}}$ can be calculated. These are found to be $7.06 \times 10^2 \text{ (M}^{-1}\text{s}^{-1})$ and $2.13 \times 10^2 \text{ (M}^{-1}\text{s}^{-1})$ respectively for L = IDA. Resolution of rates for PdEDTA(OH)- CN^- reaction has not been possible due to lack of information about the stability constants of PdEDTA(OH) complexes.

IV.4.2.2 Dependence of ionic strength on the Forward rate

The rates of forward reaction increases with increase in ionic strength (Table IV.5). The value of $Z_A Z_B$ obtained from the slope of plot of k_f versus $\sqrt{I} / (1 + \sqrt{I})$ (I = Ionic strength) are close to 4 and 2 for EDTA and IDA respectively (Fig. IV.8).

IV.4.2.3 Activation parameters

The forward reaction for both the systems are studied over a temperature range of 25-45°C. The activation parameters for

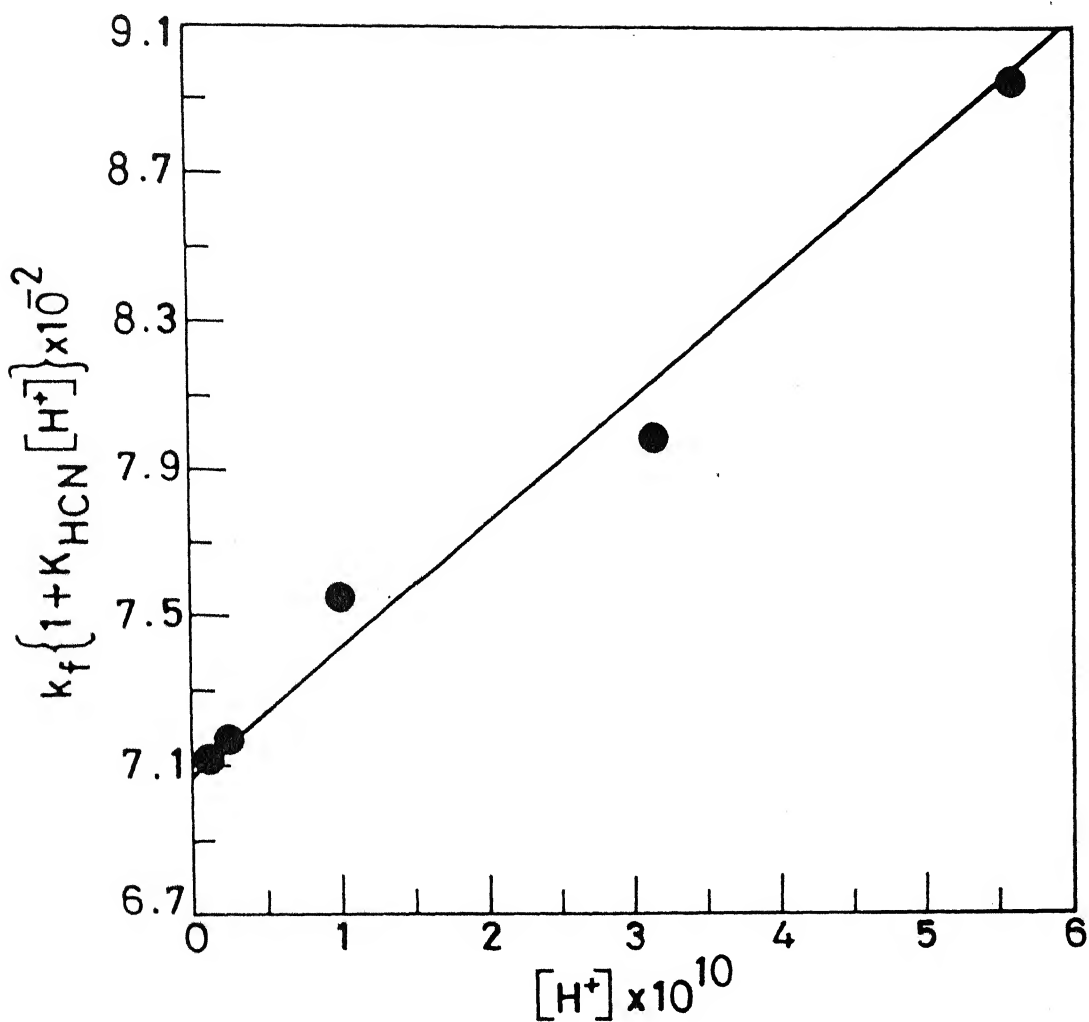


Fig.IV.7 Resolution of rate constants due to reactions of $C\bar{N}$ and HCN with PdIDA.

Table IV.5. Effect of Ionic strength on the rate of forward reaction at 25°C.

A. $[\text{PdEDTA}(\text{OH})^{3-}] = 8.0 \times 10^{-5} \text{M}$, $[\text{CN}^-] = 1.5 \times 10^{-2} \text{M}$ and $\text{pH} = 11.5$.

B. $[\text{PdIDA}] = 8.0 \times 10^{-5} \text{M}$, $[\text{CN}^-] = 7.5 \times 10^{-3} \text{M}$ and $\text{pH} = 11.0$.

	$\text{I, M}(\text{NaClO})_4$	k_{obs}	$k_f, 10^{-2}, \text{M}^{-1} \text{s}^{-1}$
A.	0.08	4.61	3.07
	0.1	4.89	3.26
	0.15	6.58	4.39
B.	0.1	5.27	7.03
	0.15	5.59	7.45
	0.20	9.65	12.87

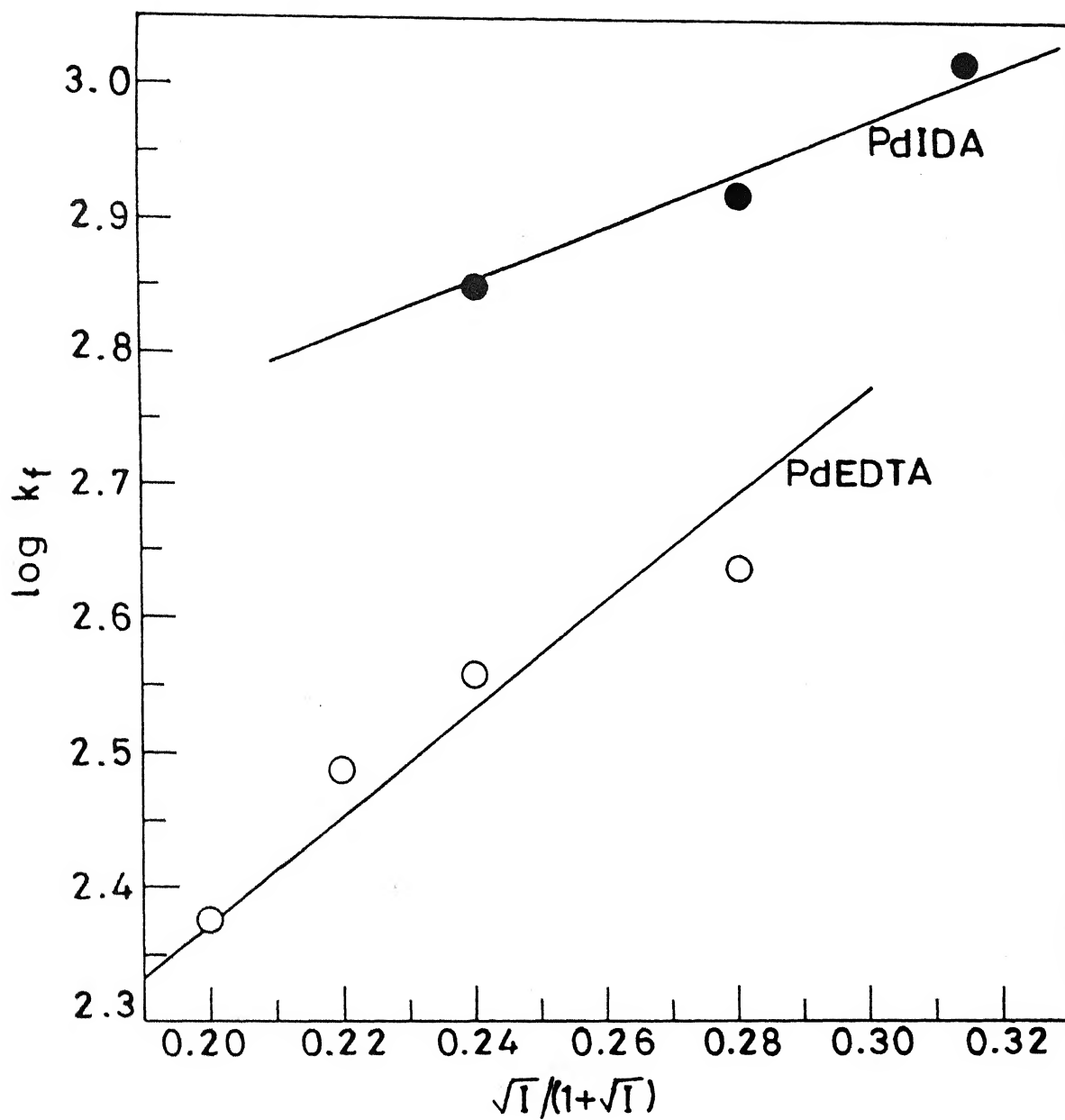


Fig.IV.8 Effect of ionic strength on the rate of forward reaction. The reaction conditions are given in Table IV.5.

both the situations i.e. where the order dependence in $[\text{CN}^-]$ is one and zero, are determined. Data are given in Table IV.6.

IV.4.3 Kinetics of Reverse Reaction

The reverse reaction between $\text{Pd}(\text{CN})_4^{2-}$ and L^{n-} ($\text{L}^{n-} = \text{EDTA}^{4-}$ and IDA^{2-}) taken in large excess has not been possible even at a higher temperature of 50°C . This may be due to the large difference between the stability constants of the reactants and products. ($K_{\text{PdEDTA}} = 10^{18.5^{12}}$, $K_{\text{PdIDA}} = 10^{4.55^{16}}$ and β_4 for $[\text{Pd}(\text{CN})_4]^{2-} = 10^{63.20}$).

IV.4.4 Discussion

The kinetic data in case of $\text{PdEDTA}(\text{OH})$ giving rise to zero order dependence in cyanide can be explained if a slow dissociation of $\text{PdEDTA}(\text{OH})$ is assumed according to eqn. (1) (vide infra). The order dependence in cyanide in case of EDTA at higher concentration has been found to be only one whereas in IDA case only a first order dependence in $[\text{CN}^-]$ has been found. An unequivocal mechanism for the substitution reaction based only on the forward rate data is not possible. But some guidance is available from the studies of few similar systems studied earlier. Substitution reactions on $\text{Ni}(\text{II})$ centre represented by eqn. (10) have been studied extensively.^{7,21-26}

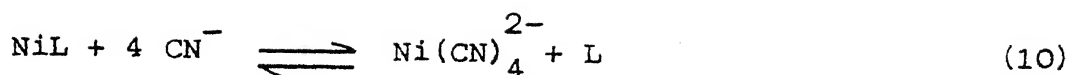
Table IV.6. Activation parameters for the forward reactions.

A. $[\text{PdEDTA}(\text{OH})]^{3-} - \text{CN}^-$ system:

	Zero order	First order
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	15.1 ± 1.1	10.2 ± 1.4
$\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$	-235 ± 2	-191 ± 2

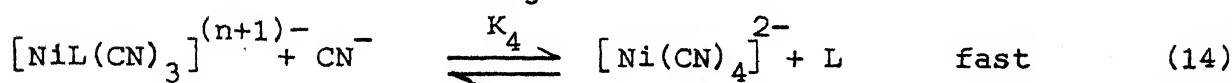
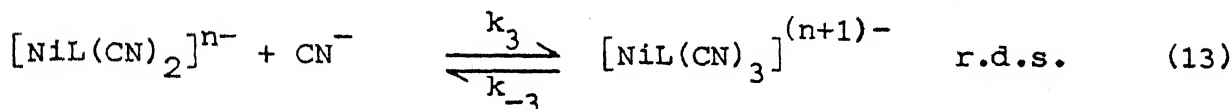
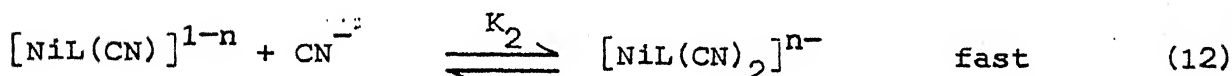
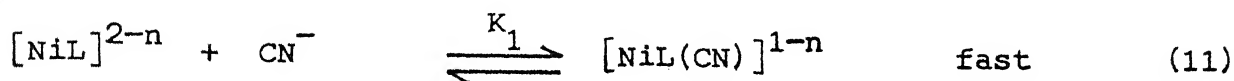
B. $[\text{PdIDA}] - \text{CN}^-$ system:

$\Delta H^\ddagger (\text{kJ mol}^{-1})$	-	37.9 ± 2.5
$\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$	-	-191 ± 2



(L = Aminocarboxylates, polyamines and macrocyclic ligands)

The forward reactions show a variable order dependence in cyanide ions. The reverse reactions, on the other hand, exhibit an inverse first order dependence in cyanide. The study of kinetics of forward and reverse reactions makes it possible to propose a four step mechanism (eqn. 11-14) in which the third step is the rate-determining one.

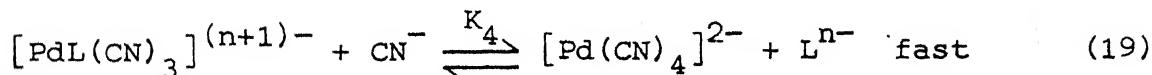
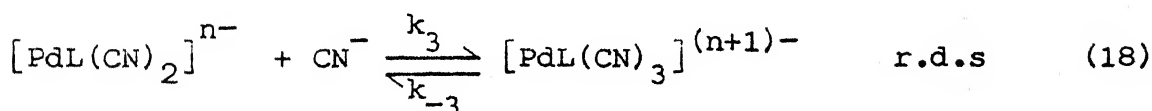
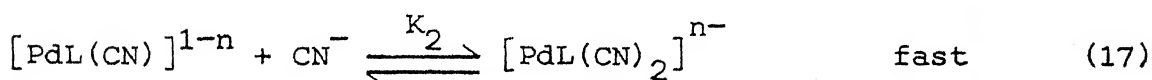
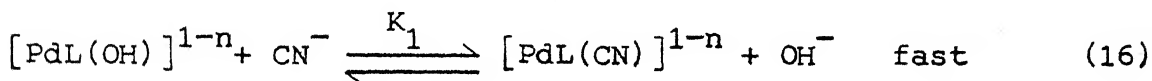
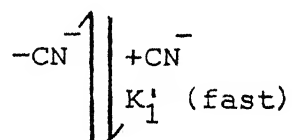
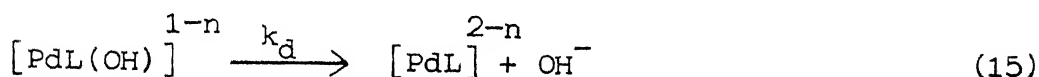


Other evidences such as activation parameters and the effect of ionic strength provide further support to this mechanism.

Of late, studies on exchange of aminocarboxylates complexed to Fe(III)²⁶⁻³¹ (chapter II) and Mn(III) centres³²⁻³⁴ (chapter III) by cyanide ions show the occurrence of a five step and six step sequence respectively where the step preceding the last step is the rate-determining one in each case.

More recently, substitution reaction between Par (Par = 4-(2-pyridylazo)resorcinol) complexed to Pd(II) by cyanide ions has been studied in our laboratory.¹⁰ Both the forward and reverse rate studies again show the penultimate step to be the rate-determining in the four step mechanism proposed.

With this information and back ground at our disposal, we venture to suggest a mechanism for PdL-CN⁻ exchange reactions (L = EDTA and IDA) on similar lines which is given from equations (16-19).



Reactions involving slow dissociation of hydroxyl ion in the first step (similar to equation 15) has been shown to occur in FeHIDA(OH)₂-CN⁻ and FeTHA(OH)₂-CN⁻ reaction systems investigated

earlier by us.^{30,32} In case of EDTA reaction this is expected because bond breaking is involved in eqn.(15) whereas in case of eqn.(18), the process is associative. The effect of ionic strength on the forward reaction rates gives a value of $Z_A Z_B \approx 4$ for EDTA and ≈ 2 for IDA systems. Both the values are found to be consistent with the rate-determining step in the proposed multistep mechanism. So it can be said with some confidence that the proposed mechanism may indeed be valid for the systems under investigation too.

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CHAPTER V

KINETICS AND MECHANISM OF OXIDATION OF POLYALKYLENE- POLYAMINES BY HEXACYANOFERRATE(III)

ABSTRACT

The kinetics of the reaction between polyalkylenepolyamines (abbrev. P) viz. Diethylenetriamine (Dien), Triethylenetetraamine (Trien) and Tetraethylenepentaamine (Tet) have been investigated spectrophotometrically at 420 nm (λ_{\max} of $[\text{Fe}(\text{CN})_6]^{3-}$). The reaction conditions are: pH = 10.5, I = 0.1M(KNO_3) and temp. = $30 \pm 0.1^\circ\text{C}$. The reactions exhibit first-order dependence each in hexacyanoferrate(III) and the respective polyalkylenepolyamines (P), second order overall. The rate expression is given by

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k_2[\text{Fe}(\text{CN})_6^{3-}][\text{P}]_T \quad (1)$$

The rate constants increase in the pH range 8.5 - 11.85, for all three reactions. The reactive species in the above pH range are $[\text{Fe}(\text{CN})_6]^{3-}$ on the one hand and H_2P^{2+} , HP^+ and P on the other. From the pH dependence data, it has been possible to resolve the

rate constants due to reactions of $[\text{Fe}(\text{CN})_6]^{3-}$ with P, HP^+ and H_2P^{2+} in all the three cases. The effect of ionic strength is found to be negligible at the chosen reaction conditions. The activation parameters are also evaluated and have been cited in support of the proposed mechanism. An electron transfer from $[\text{Fe}(\text{CN})_6]^{3-}$ to the substrate(s), during the oxidation of the latter, is proposed. The stoichiometry of the reactions between polyalkylenepolyamines and $[\text{Fe}(\text{CN})_6]^{3-}$ is found to be 1:1 for each case.

V.2 Introduction

Oxidations of aliphatic primary, secondary and tertiary amines by various oxidants have been investigated and reviews covering the oxidation of amines have appeared before.^{1,2} Some reactions of this class are cited here as examples. Oxidations of $\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{NH}_2$ and $\text{CH}_3 \cdot (\text{CH}_2)_{12} \cdot \text{NH}_2$ by 3,4-disubstituted, 1-methylpyrimidol 4-deazotoxoflavins have been studied.³ PdCl_2 and AuCl_3 are known to oxidise primary amines.⁴ Oxidations of aliphatic secondary amines viz. $(\text{R} \cdot \text{CH}_2 \cdot \text{CH}_2)_2 \cdot \text{NH}$ ($\text{R} = \text{Et}, \text{Pr}$) by peroxydisulphate have been reported.⁵ Chalatykyan and Beiteryan⁶ have investigated oxidations of Et_3N by benzoylperoxide. Kovtun et al.⁷ have studied the oxidation kinetics of Et_3N and Bu_3N by molecular oxygen.

Oxidants viz. rutheniumtetroxide⁸, sodiumpercarbonate⁹, azohydroperoxide¹⁰ and diphenylselenic anhydride¹¹ have been used for amine oxidations. Ruthenium promoted oxidation of amines has been investigated by Taube.¹² Recently, oxidation of aliphatic amines by MnO_4^- ion has been attempted.¹³ But to the best of our knowledge the oxidations of polyalkylenepolyamines have not been attempted so far.

For the last few years investigations on substitution reactions of mono(aminocarboxylato)hydroxoferrate(III) complexes with cyanide ions have been carried out in our laboratory.¹⁴⁻¹⁸ A three stage reaction sequence has been proposed for this class of reactions as given below:

First stage : Formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ from $[\text{FeL}(\text{OH})]^{2-n}$

Second stage: Conversion of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$

Third stage : Oxidations of L^{n-} (polyaminocarboxylate anions), released in the first stage, by the $[\text{Fe}(\text{CN})_6]^{3-}$.

Oxidation reactions of polyaminocarboxylate anions viz. EDTA^{4-} , EGTA^{4-} and IDA^{2-} ¹⁹ with the oxidant $[\text{Fe}(\text{CN})_6]^{3-}$ have been investigated by other workers earlier whereas oxidation kinetics of DTPA^{5-} has been carried out in our laboratory.²⁰

We intend to study the reactions of cyanide ions with polyalkylenepolyamino-ferrate(III) complexes. During preliminary investigation we noticed that hexacyanoferrate(III) produced in the reaction (second stage) oxidises polyamines. It is known to oxidise the polyaminocarboxylates as well.^{19,20} Therefore, it has been considered worthwhile to study the kinetics of oxidations of a few polyalkylenepolyamines viz. diethylenetriamine (Dien), triethylenetetraamine (Trien) and tetraethylenepentaamine (Tet) in order to obtain a better understanding for this class of reactions. Oxidation of trien by hexacyanoferrate(III) has been reported by us before.²¹

V.3 Materials and Methods

Potassium hexacyanoferrate(III) (AR, SDS), Diethylenetriamine (Eastman Kodak, USA), Triethylenetetraamine (AR, Fluka), Tetraethylenepentaamine (AR, BDH, England) and Sodium cyanide (May and Baker, England) have been used for this study. Standardisation of sodium cyanide is carried out argentometrically.²² Sodium hydroxide or perchloric acid has been used to maintain pH at any desired value. The pH meter is standardised with standard BDH buffers, potassium nitrate or sodium perchlorate (G.R., Sarabhai, M.) is used to maintain the ionic strength. Triple distilled water has been used for the preparation of all solutions.

A Shimadzu double beam spectrophotometer model UV-240, fitted with a circulatory arrangement for thermostating the cell compartment, has been used for kinetic study and for recording the spectral changes. The temperature could be controlled to within $\pm 0.1^\circ\text{C}$. An Elico digital pH meter model LI-120 has been used for pH measurements.

V.4 Kinetic Measurements

The reaction between polyalkylenepolyamines (P) and hexacyanoferrate(III) is followed at 420 nm (broad band of $\text{Fe}(\text{CN})_6^{3-}$, $\epsilon = 1020 \text{ M}^{-1}\text{cm}^{-1}$) at $30 \pm 0.1^\circ\text{C}$. The other conditions for all the three reactions are $\text{pH} = 10.5 \pm 0.02$ and $I = 0.1\text{M}(\text{KNO}_3)$. The reactions are studied under pseudo-first-order conditions ($[\text{P}] \gg [\text{oxidant}]$). Solutions of hexacyanoferrate(III) and polyalkylenepolyamines [P] are equilibrated at the desired temperature for about 30 minutes before mixing. The ionic strength and pH are adjusted each time before equilibrating the reactants.

The pseudo-first-order rate constants are calculated from plots of $\log C_A$ versus time where C_A refers to $[\text{K}_3\text{Fe}(\text{CN})_6]$ remaining at any time t . These rate constants are given in Table V.1. The dependence of pseudo-first-order rate constants on concentrations of Dien, Trien and Tet is shown in Fig. V.1. The absorbance changes are observed for at least 70% of the reaction.

Table V.1. Evaluation of pseudo-first-order rate constants and overall second order rate constants for the reactions of $[\text{Fe}(\text{CN})_6]^{3-}$ with $[\text{P}]$. The reactions conditions are: $[\text{Fe}(\text{CN})_6^{3-}] = 5.0 \times 10^{-4} \text{ M}$, $\text{pH} = 10.5 \pm 0.02$, $\text{temp.} = 30 \pm 0.1^\circ \text{C}$ and $\text{I} = 0.1 \text{ M} (\text{KNO}_3)$.

$[\text{Dien}]_{\text{T}}, 10^3, \text{M}$	$k_{\text{obs}}, 10^5, \text{s}^{-1}$	$k_{\text{f}} = k_{\text{obs}} / [\text{P}]_{\text{T}}, 10^3, \text{M}^{-1} \text{s}^{-1}$
5.0	3.2	6.4
7.5	4.6	6.1
10.0	7.3	7.3
12.5	8.3	6.6
15.0	11.1	7.4
<hr/>		
$k_{\text{f}}(\text{av}) = (6.76 \pm 0.51) \times 10^{-3}, \text{M}^{-1} \text{s}^{-1}$		
$[\text{Trien}]_{\text{T}}, 10^3, \text{M}$	$k_{\text{obs}}, 10^3, \text{s}^{-1}$	$k_{\text{f}}, 10^1, \text{M}^{-1} \text{s}^{-1}$
5.0	0.9	1.8
7.5	1.3	1.7
10.0	1.8	1.8
12.5	2.2	1.8
15.0	2.6	1.7
<hr/>		
$k_{\text{f}}(\text{av}) = (1.77 \pm 0.18) \times 10^{-1}, \text{M}^{-1} \text{s}^{-1}$		
$[\text{Tet}]_{\text{T}}, 10^3, \text{M}$	$k_{\text{obs}}, 10^3, \text{s}^{-1}$	$k_{\text{f}}, 10^1, \text{M}^{-1} \text{s}^{-1}$
5.0	0.8	1.6
7.5	1.4	1.9
10.0	1.7	1.7
15.0	2.6	1.7
<hr/>		
$k_{\text{f}}(\text{av}) = (1.73 \pm 0.11) \times 10^{-1}, \text{M}^{-1} \text{s}^{-1}$		

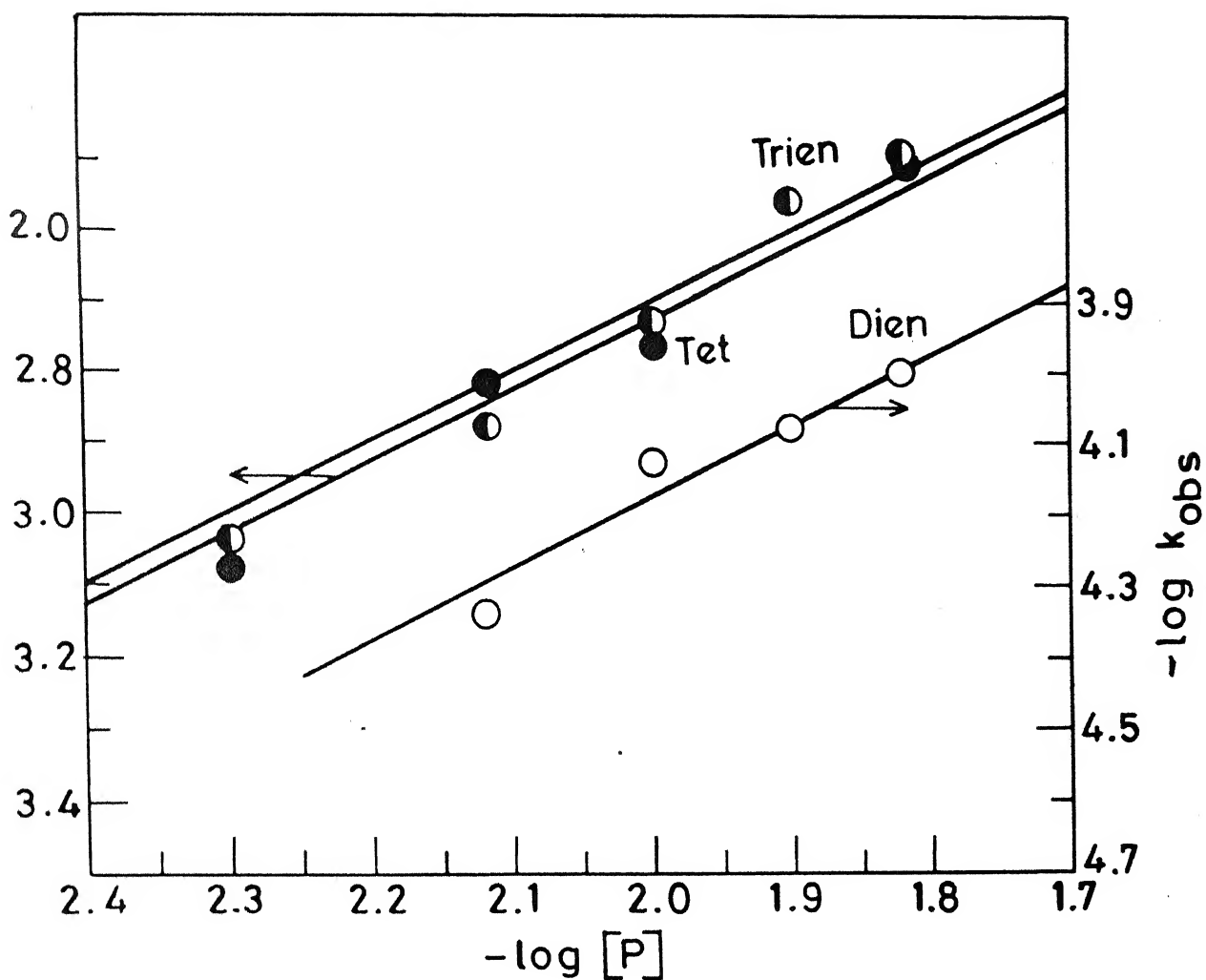


Fig.V.1 The dependence of pseudo-first-order rate constants on $[P]$. Reaction conditions are given in Table V.1.

V.4.1 Dependence of reaction rate on pH

The reactions have been studied over the pH range 8.5-11.85. The rate constants at various pH are reported in Table V.2. A plot of $\log k_{\text{obs}}$ versus pH is shown for all the three systems in Fig. V.2. The species distribution of the three amines as a function of pH are given in Fig. V.3, Fig. V.4 and Fig. V.5. They have been calculated on a Dec-10 computer using a programme developed by Perrin and Sayce.²³ The predominant species of the ligands in the pH range of interest are H_2P^{2+} , HP^+ and P in varying proportion. The protonation constants of different species of all the three ligands are listed in Table V.3.²⁴ In all the three cases it is seen that the reaction rate increases linearly with increase in pH and then levels off at $\text{pH} \gg 11$. Below pH 8.5 the rate is found to be extremely slow. The rate can be expressed by equation (2).

$$\text{Rate} = k_f [\text{Fe}(\text{CN})_6^{3-}] [\text{P}]_T \quad (2)$$

In equation (2), the concentration term $[\text{P}]_T$ includes unprotonated and protonated forms of P. In this pH range the hexacyanoferrate(III) exists as $[\text{Fe}(\text{CN})_6]^{3-}$ only. The rate of oxidation of P by $[\text{Fe}(\text{CN})_6]^{3-}$ is, therefore, given by equation (3).

Table V.2. Effect of varying pH on the rate of reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ with P; $[\text{Fe}(\text{CN})_6^{3-}] = 5 \times 10^{-4} \text{ M}$,
temp. = $30 \pm 0.1^\circ \text{C}$ and $I = 0.1 \text{ M}(\text{NaClO}_4)$.

$$[\text{Dien}]_T = 1.0 \times 10^{-2} \text{ M}$$

pH	$k_{\text{obs}}, 10^5, \text{M}$	$k_f = k_{\text{obs}} / [\text{P}], 10^3, \text{M}^{-1} \text{s}^{-1}$
8.60	5.85	5.85
8.80	6.31	6.31
9.50	6.86	6.86
9.75	7.16	7.16
10.0	7.34	7.34
10.5	7.34	7.34

$$[\text{Trien}]_T = 1.0 \times 10^{-2} \text{ M}$$

pH	$k_{\text{obs}}, 10^3, \text{M}$	$k_f = k_{\text{obs}} / [\text{P}], 10^1, \text{M}^{-1} \text{s}^{-1}$
8.5	1.35	1.35
9.0	1.45	1.45
9.5	1.58	1.58
10.0	1.66	1.66
10.5	1.79	1.79
11.0	1.86	1.86
11.85	1.88	1.88

...contd.

Table V.2(contd.)

$$[\text{Tet}]_{\text{T}} = 1.0 \times 10^{-2}, \text{M}$$

pH	$k_{\text{obs}}, 10^3, \text{s}^{-1}$	$k_{\text{f}}, 10^1, \text{M}^{-1} \text{s}^{-1}$
8.5	1.12	1.12
9.0	1.44	1.44
9.5	1.55	1.55
10.0	1.66	1.66
10.5	1.71	1.71
11.0	1.79	1.79

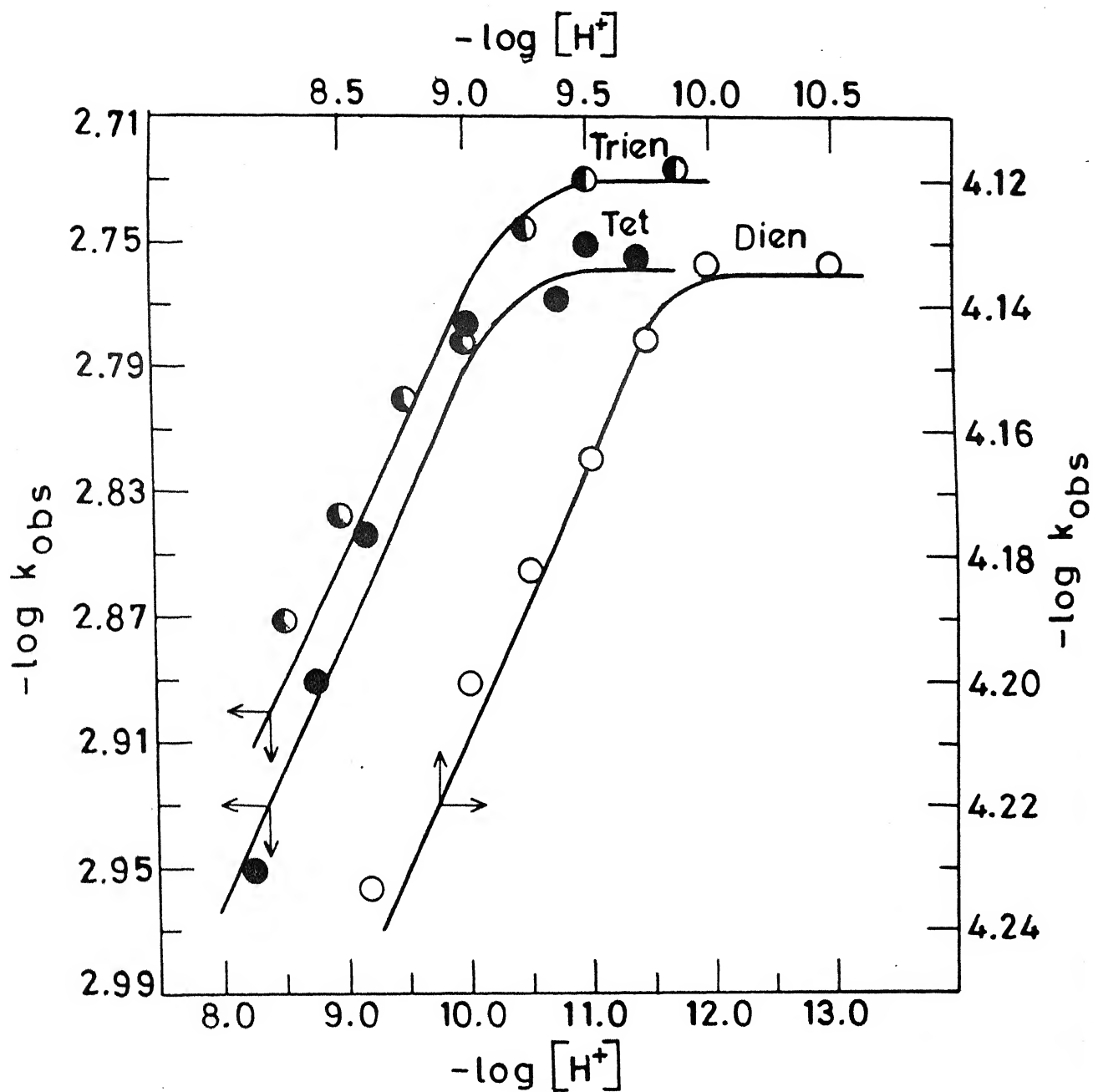


Fig.V.2

Effect of pH on the reaction of P with $[Fe(CN)_6]^{3-}$. Reaction conditions are given in Table V.2

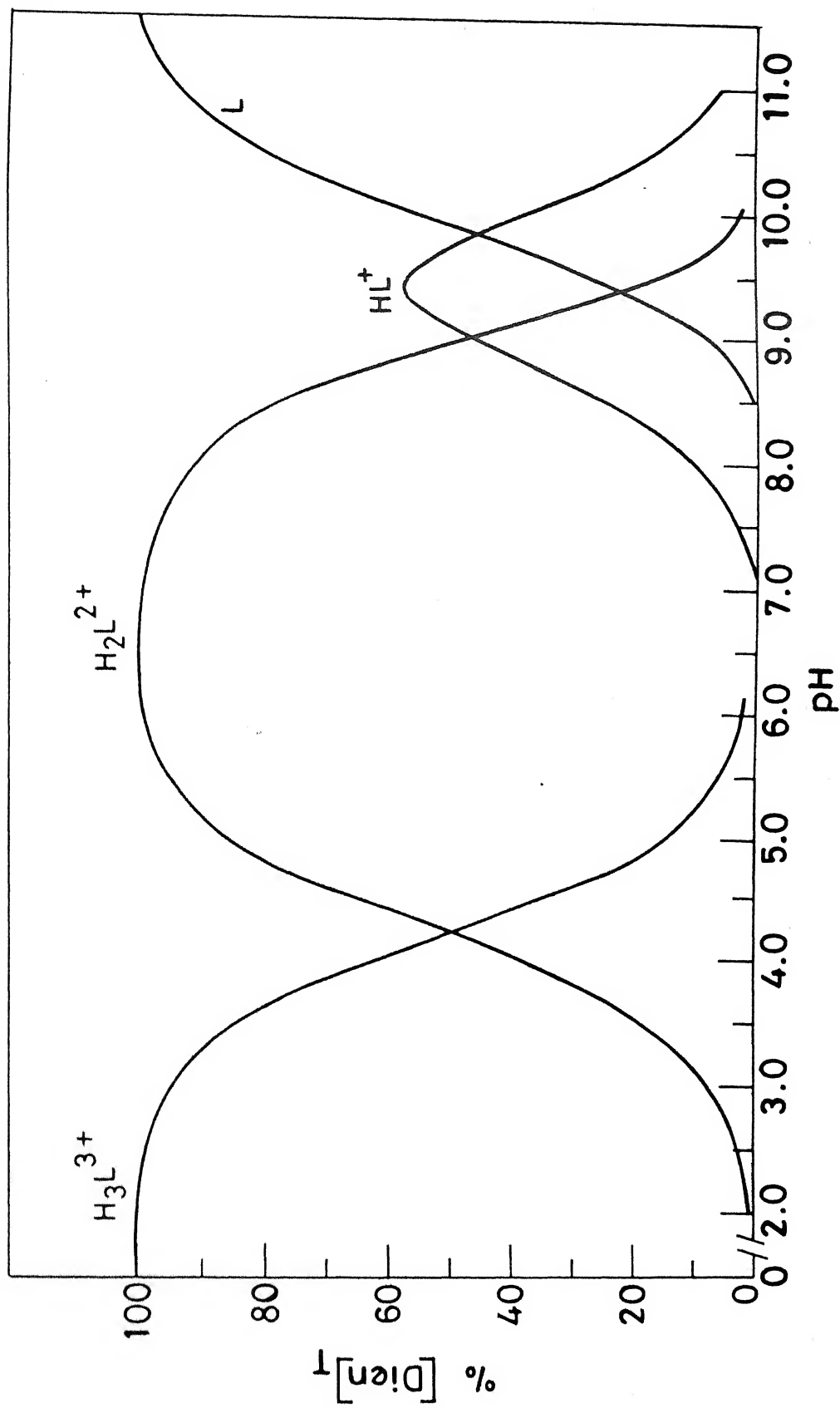


Fig.V.3 Species distribution of dien as a function of pH; $[Dien] = 5 \times 10^{-4} M$.

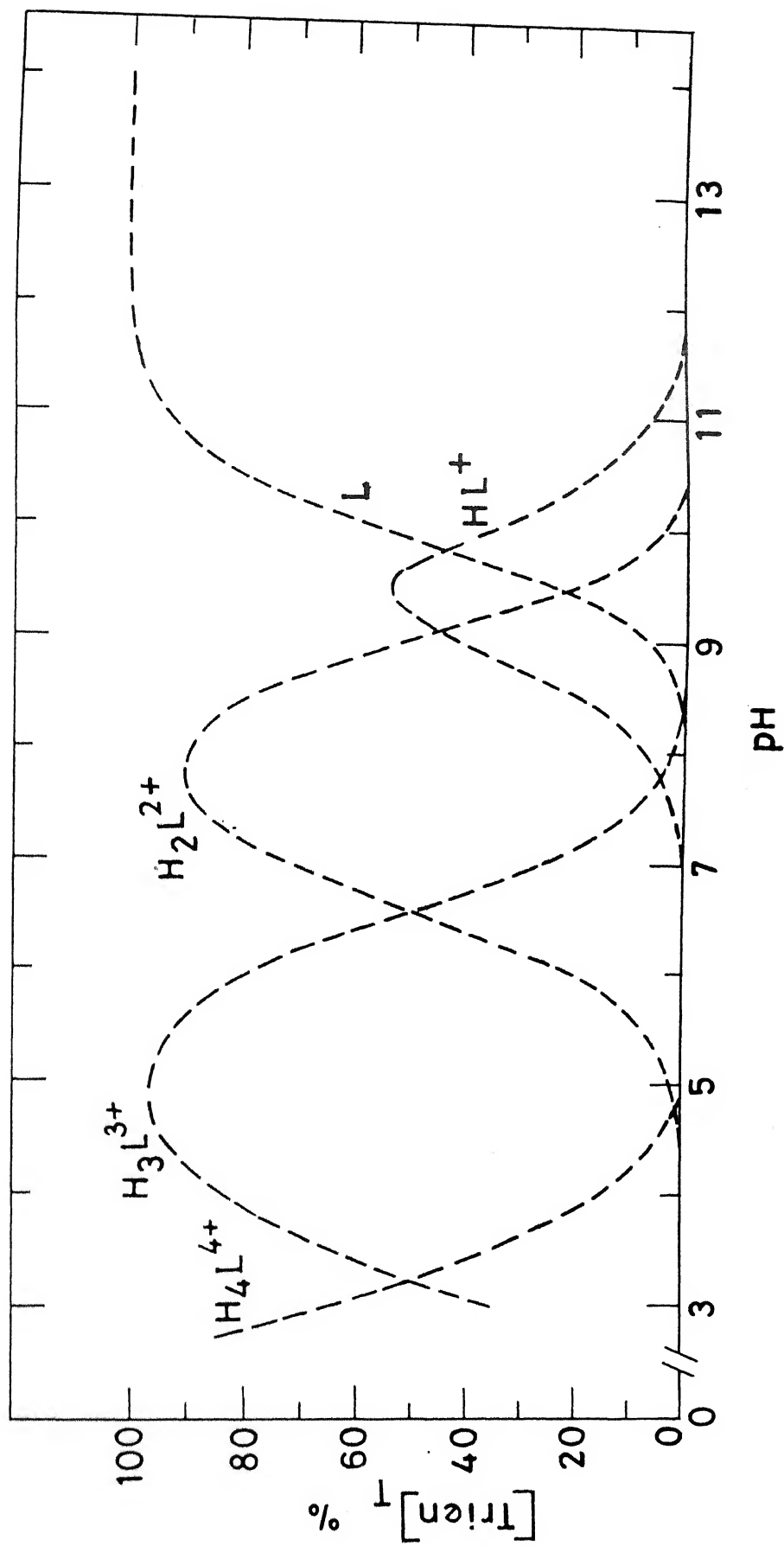


Fig. V.4 Species distribution of Trien as a function of pH; $[\text{Trien}] = 5 \times 10^{-4} \text{ M}$

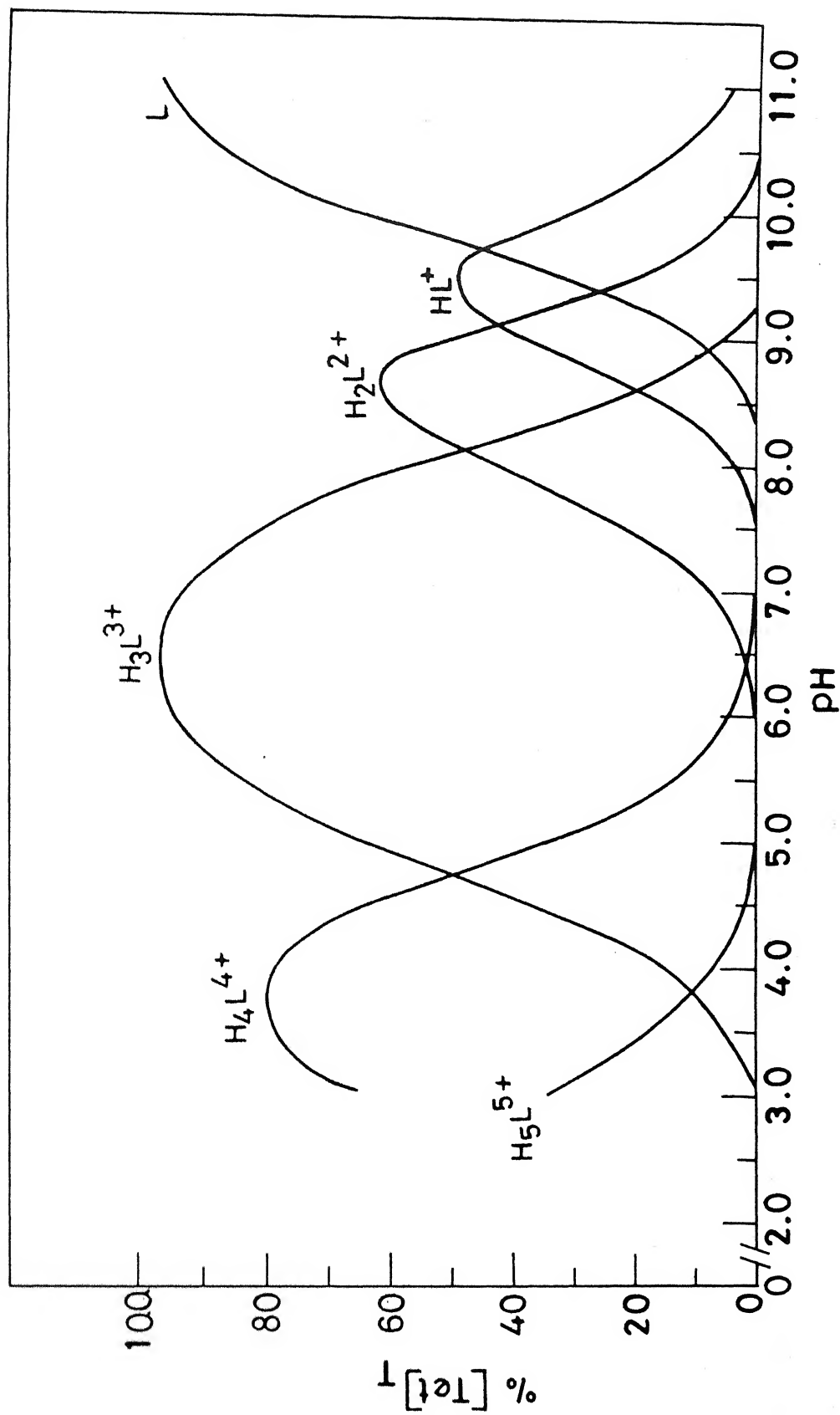


Fig. V.5 Species distribution of Tet as a function of pH; $[Tet] = 5 \times 10^{-4}$ M.

Table V.3. Protonation constants ($\log K_H$) of polyalkylene-polyamines at 25°C and $I = 0.1M(KCl)$.²⁴

Polyalkylene-polyamines	HP	H ₂ P	H ₃ P	H ₄ P	H ₅ P
Dien	9.79	8.95	4.22	-	-
Trien	9.8	9.08	6.55	3.25	-
Tet	9.68	9.10	8.08	4.72	2.98

$$\begin{aligned}
 \text{Rate} &= [\text{Fe}(\text{CN})_6^{3-}] (k_1[\text{P}] + k_2[\text{HP}^+] + k_3[\text{H}_2\text{P}^{2+}]) \\
 &= [\text{Fe}(\text{CN})_6^{3-}] (k_1[\text{P}] + k_2K_1[\text{H}^+][\text{P}] + k_3K_1K_2[\text{H}^+]^2[\text{P}]) \\
 &= [\text{Fe}(\text{CN})_6^{3-}][\text{P}] (k_1 + k_2K_1[\text{H}^+] + k_3K_1K_2[\text{H}^+]^2) \quad (3)
 \end{aligned}$$

where k_1 , k_2 and k_3 are rate constants due to P , HP^+ and H_2P^{2+} species respectively, while K_1 and K_2 are the first and second protonation constants of P . Comparing eqns.(2) and (3), eqn.(4) is obtained.

$$k_f \frac{[\text{P}]_T}{[\text{P}]} = k_1 + k_2K_1[\text{H}^+] + k_3K_1K_2[\text{H}^+]^2 \quad (4)$$

$$\text{where } \frac{[\text{P}]_T}{[\text{P}]} = 1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+]^2 \quad (5)$$

At $\text{pH} > 10.0$ the terms containing $[\text{H}^+]^2$ can be neglected. So equation (4) is simplified to equation (6).

$$k_f (1 + K_1[\text{H}^+]) = k_1 + k_2K_1[\text{H}^+] \quad (6)$$

In the higher pH region a plot of left hand side of equation (6) versus $[\text{H}^+]$ is linear. The slope of this line gives the value of k_2 (i.e. the reaction rate between $[\text{Fe}(\text{CN})_6]^{3-}$ and HP^+). The intercept of the linear plot gives the value of rate constant k_1 (i.e. the rate constant for reaction between $[\text{Fe}(\text{CN})_6]^{3-}$ and P). On transformation of equation (4) followed by taking logarithm

one gets equation (7).

$$\begin{aligned} \log \left[\frac{k_f}{[H^+]} (1 + K_1[H^+] + K_1K_2[H^+]^2 - k_1-k_2[H^+]) \right] \\ = \log (k_3K_1K_2) + \log [H^+] \end{aligned} \quad (7)$$

Plots of left hand side of equation (7) versus $\log [H^+]$ are found to be linear in all the three cases as shown in Fig. V.6, Fig.V.7 and Fig. V.8. The slopes of these lines are close to one and the intercept ($\log k_3K_1K_2$) gives an estimated value of k_3 . The rate constants k_1 , k_2 and k_3 for all the three systems are given in Table V.4. It is observed that the rate (k_3) below pH 8.5 is extremely slow in all the three cases studied here.

V.4.2 Effect of Ionic strength on rate

The effect of ionic strength on the reaction rate in the range $I=(0.1-0.35)M$, is found to be negligible in each case as expected from the reaction of $[Fe(CN)_6]^{3-}$, a charged ion, with polyalkylenepolyamines an uncharged P existing at the chosen reaction conditions.

V.4.3 Activation parameters

Activation parameters for the reactions have been determined from the Arrhenius plots in the temperature range 25-45°C and the values are listed in Table V.5.

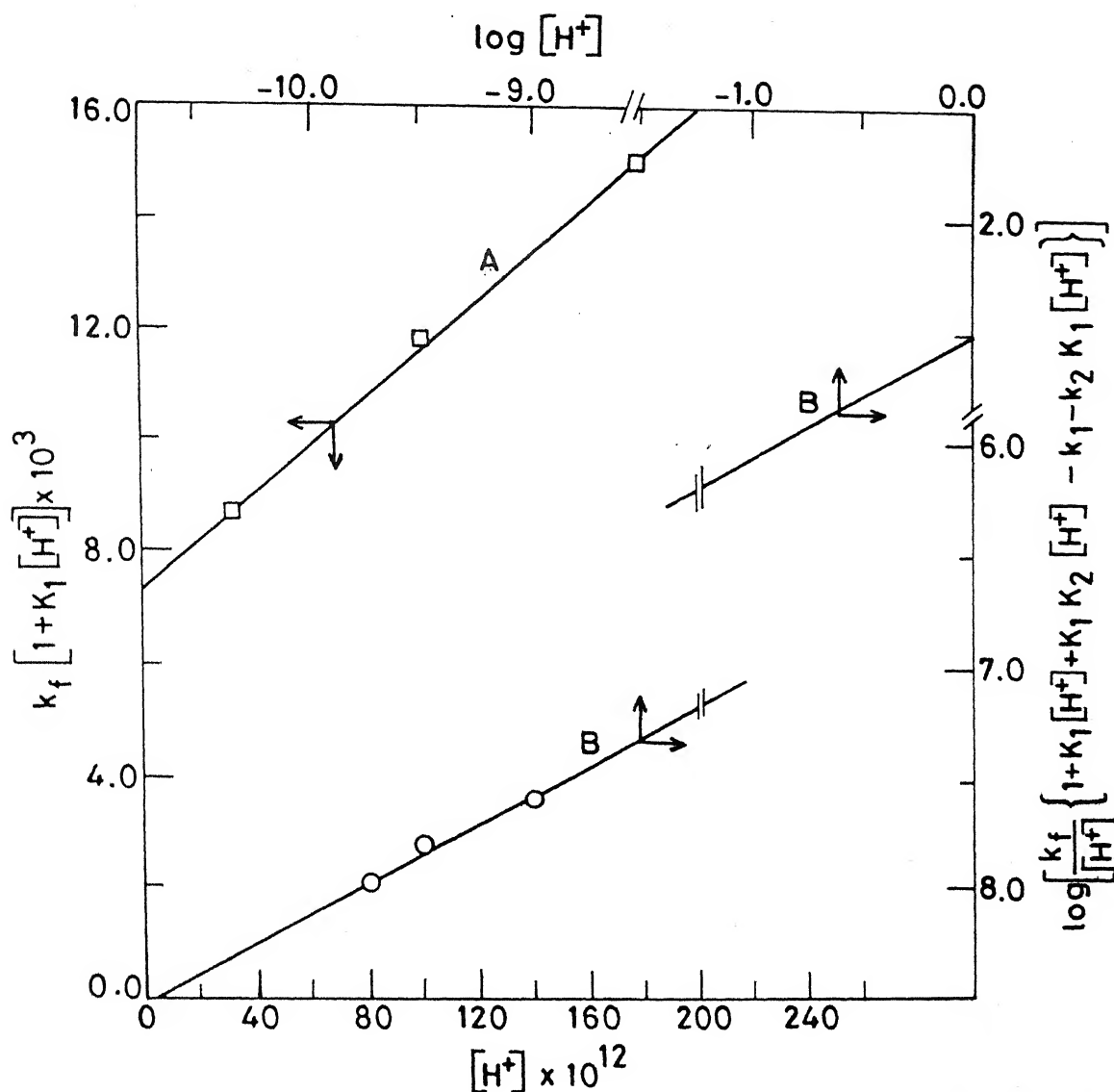


Fig.V. 6 Plot of resolution of rate constants i.e $\text{Fe}(\text{CN})_6^{3-}$ (k_1), $\text{Fe}(\text{CN})_6^{3-}$ (k_2), and $\text{Fe}(\text{CN})_6^{3-}$ (k_3); k_P $\text{Fe}(\text{CN})_6^{3-}$ (k_1), k_{HP^+} $\text{Fe}(\text{CN})_6^{3-}$ (k_2), and $k_{\text{H}_2\text{P}^{2+}}$ $\text{Fe}(\text{CN})_6^{3-}$ (k_3); $P = \text{Dien}$, temp = $30 \pm 0.1^\circ\text{C}$, $I = 0.1\text{M}$ (KNO_3).
A = plot of eqn.(6) and B = plot of eqn.(7).

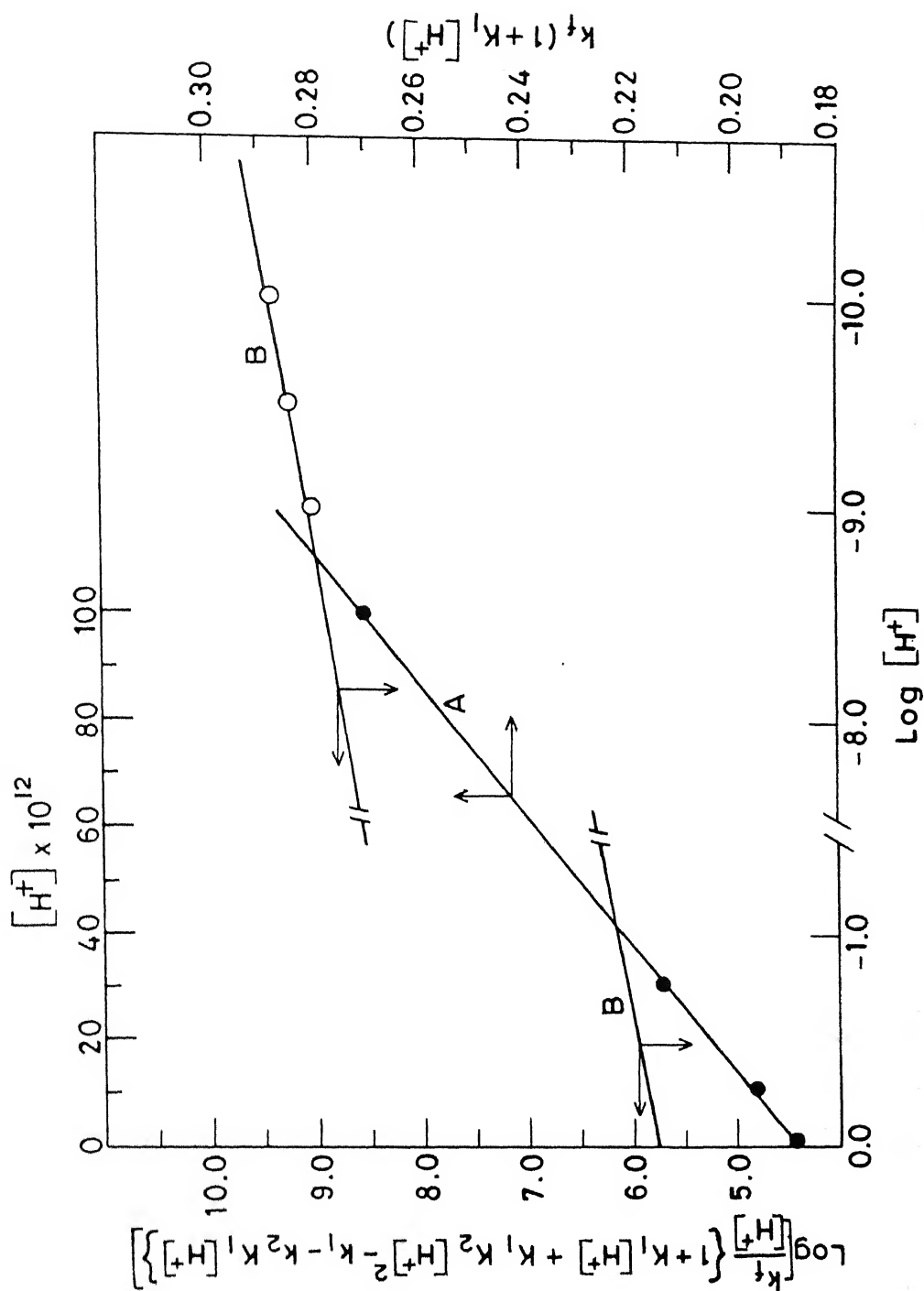


Fig.V.7 Plot of resolution of rate constants; i.e. k_t $\text{Fe}(\text{CN})_6^{3-}$ (k_1); $\text{Fe}(\text{CN})_6^{3-}$ (k_2) & k_{HP^+} $\text{Fe}(\text{CN})_6^{3-}$ (k_3); P = Trien, temp = $30 \pm 0.1^\circ\text{C}$, $I = 0.1 \text{ M}$ (KNO_3). A = plot of eqn.(6) and B = plot of eqn.(7).

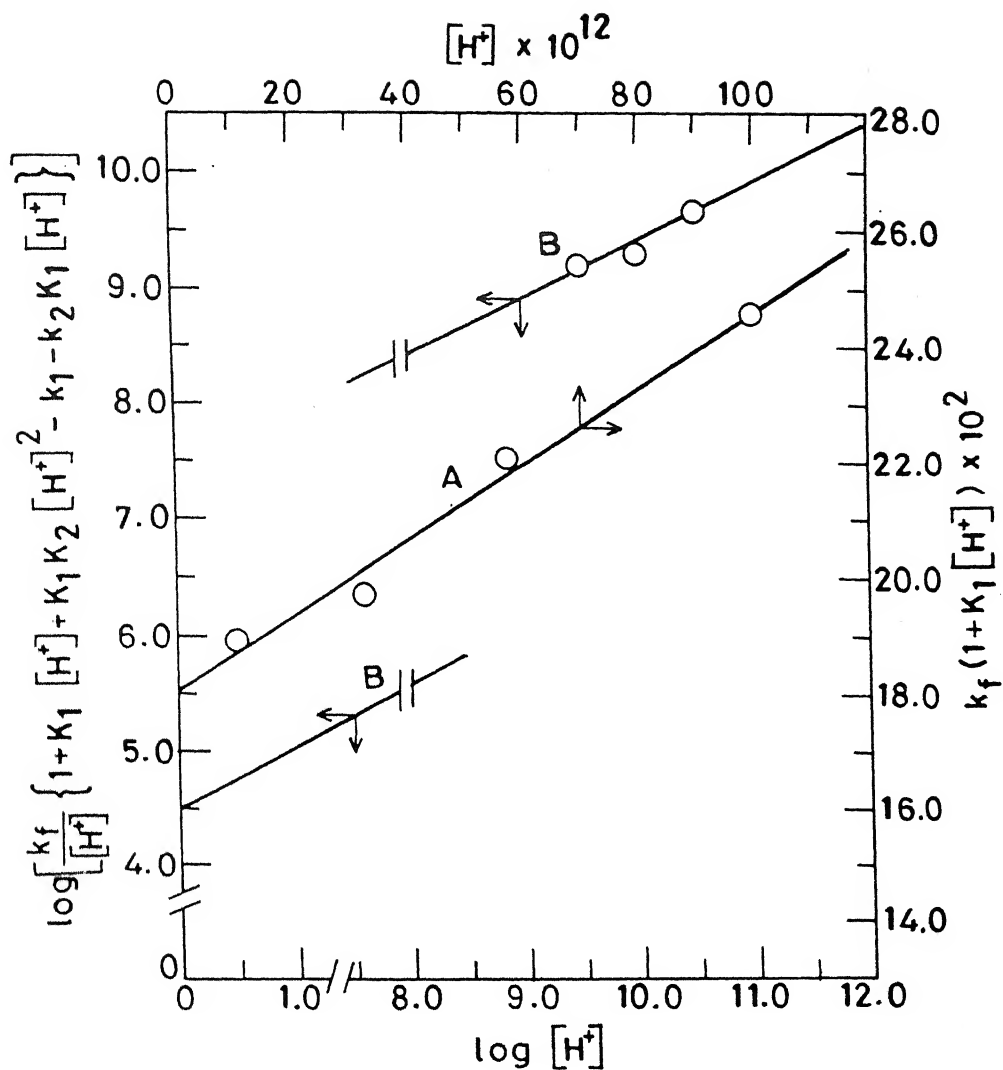


Fig.V.8 Plot of resolution of rate constants i.e.

$k_P^{Fe(CN)_6^{3-}}$ (k_1), $k_{HP^+}^{Fe(CN)_6^{3-}}$ (k_2) and $k_{H_2P^{2+}}^{Fe(CN)_6^{3-}}$ (k_3).

P = Tet, temp. = $30 \pm 0.1^\circ C$, $I = 0.1M$ (KNO_3).

A = plot of eqn. (6) and B = plot of eqn. (7).

Table V.4. Resolution of rate constants viz. k_p Fe(CN)_6^{3-} (k_1), $k_{\text{HP}^+} \text{Fe(CN)}_6^{3-}$ (k_2) and $k_{\text{H}_2\text{P}^{2+}} \text{Fe(CN)}_6^{3-}$ (k_3) for the reaction of polyalkylenepolyamines (P) with hexacyanoferrate(III).

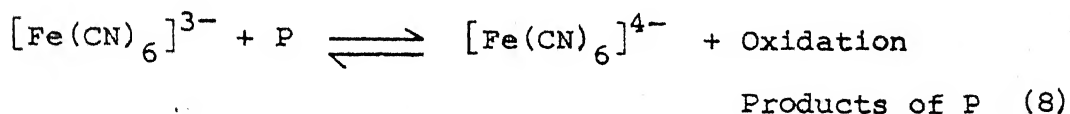
Polyalkylenepolyamines	$k_1, \text{M}^{-1}\text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$	$k_3, \text{M}^{-1}\text{s}^{-1}$
Dien	7.3×10^{-3}	6.9×10^{-3}	5.8×10^{-17}
Trien	1.9×10^{-1}	1.6×10^{-1}	7.4×10^{-14}
Tet	1.8×10^{-1}	1.5×10^{-1}	5.2×10^{-15}

Table V.5. Activation parameters for the reaction of
polyalkylenepolyamines with $[\text{Fe}(\text{CN})_6]^{3-}$

Polyalkylenepolyamines	$\Delta H^\ddagger (\text{kJ mol}^{-1})$	$\Delta S^\ddagger (\text{JK}^{-1} \text{mol}^{-1})$
Dien	41.7 ± 1.7	-286 ± 2
Trien	39 ± 2.8	-298 ± 3
Tet	16 ± 1.1	-259 ± 2

V.4.4 Determination of stoichiometry

A known excess of $[\text{Fe}(\text{CN})_6]^{3-}$ is added to a known quantity of polyalkylenepolyamine and the absorbance change at 420 nm (λ_{max} of $[\text{Fe}(\text{CN})_6]^{3-}$, $\epsilon = 1020 \text{ M}^{-1}\text{cm}^{-1}$) is determined after no further change in absorbance is observed (~ 4 days when the reaction is almost complete). In all the three cases, ratio of moles of ferri-cyanide per mole of polyamine(s) is found to 1:1. The pH of the reaction mixtures is kept at 10.5 and temp. at $20 \pm 0.1^\circ\text{C}$. The reaction may, therefore, be written as



V.5 Discussion

The kinetic data given in Table V.1 are consistent with the interaction of polyalkylenepolyamine (P) with hexacyanoferrate(III) in a bimolecular step. The reactions are found to be first order each in $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{P}]$, second order overall. The presence of cyanide in the concentration range 2.2×10^{-2} to $5.0 \times 10^{-2} \text{ M}$ does not affect the forward rate within limits of experimental error, ruling out the possibility of prior dissociation of hexacyanoferrate(III).

As the reactions are mainly between a charged $[\text{Fe}(\text{CN})_6]^{3-}$ and an uncharged species P at pH close to 10.5 the rates are expected to be independent of ionic strength as has been verified experimentally (vide infra).

The spectral changes during typical kinetic runs for all the three systems, are shown in Fig. V.9, Fig. V.10 and Fig. V.11. The general behaviour of the reaction of all the three amines are found to be similar. There is a continuous decrease in the peak height at 420 nm and 303 nm due to fall in concentration of hexacyanoferrate(III). Hexacyanoferrate(II) exhibits weak absorption bands at 322 and 260 nm, but these could not be observed because they get lost in the shoulder and peak of hexacyanoferrate(III) at 325 and 262 nm respectively. An isosbestic point at 281 nm indicates the coexistence of two species, viz. $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ during the reaction. Two specific tests for hexacyanoferrate(II) viz. the ammonium molybdate²⁵ and the thorium nitrate²⁵ tests confirm the formation of $[\text{Fe}(\text{CN})_6]^{4-}$ as one of the reaction products. The absence of any new peak points to the fact that no reaction intermediate(s) is/are present in detectable concentration. The absorption peaks of other oxidation products possibly could have been seen in the UV region, but can not be located because both $[\text{Fe}(\text{CN})_6]^{3-}$ and polyamines also absorb strongly in the same region. The identification of oxidation products of polyalkylenepolyamine has not been possible because, their separation and isolation have not been successful in spite of considerable effort.

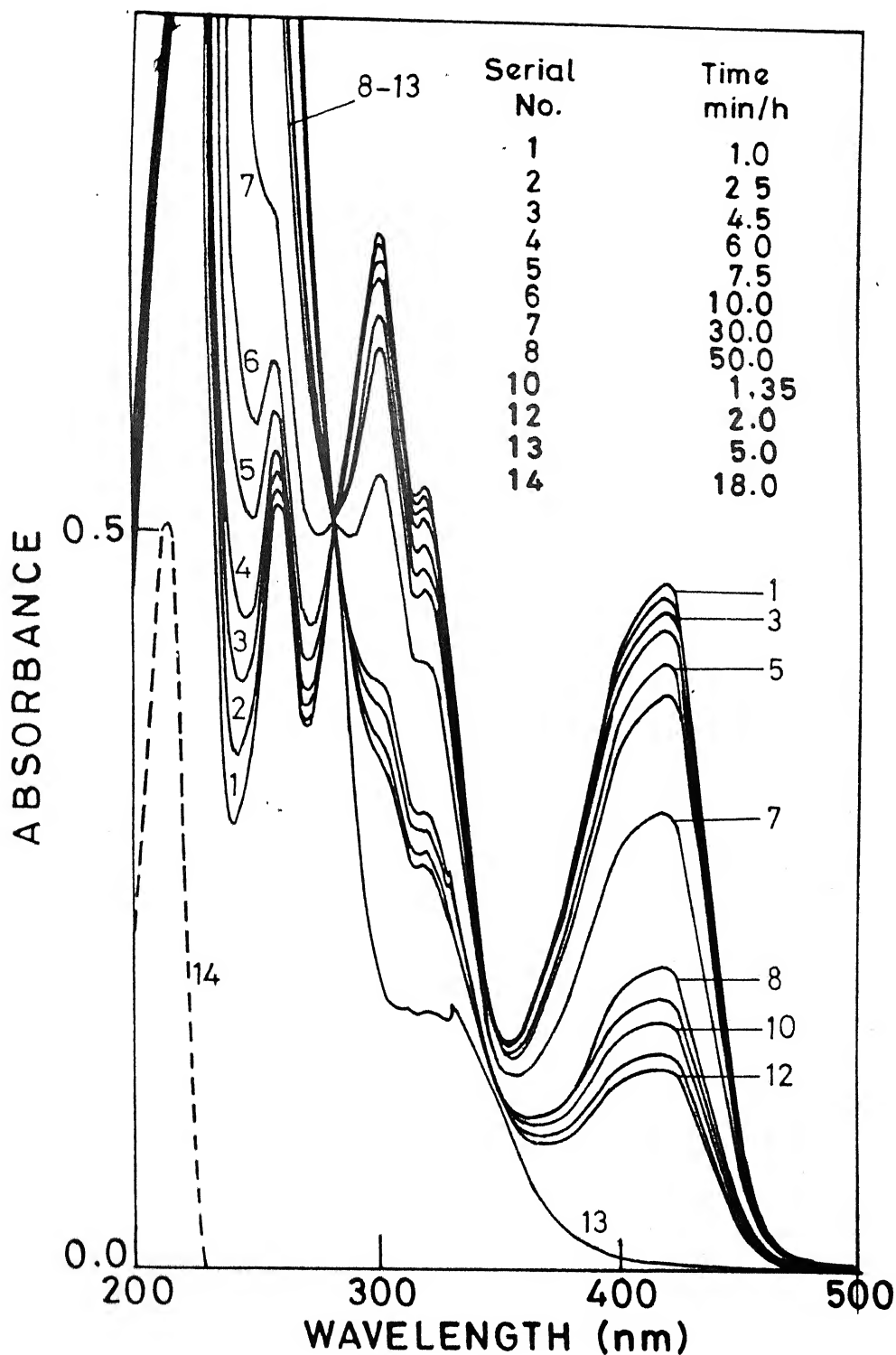


Fig.V.9 Repetitive scans of the reaction mixture during a kinetic run; $[\text{Fe}(\text{CN})_6^{3-}] = 5 \times 10^{-4} \text{ M}$, $[\text{Dien}] = 10^{-2} \text{ M}$, $\text{pH} = 10.5$, $I = 0.1 \text{ M} (\text{KNO}_3)$ and $\text{temp.} = 25 \pm 0.1^\circ \text{C}$.

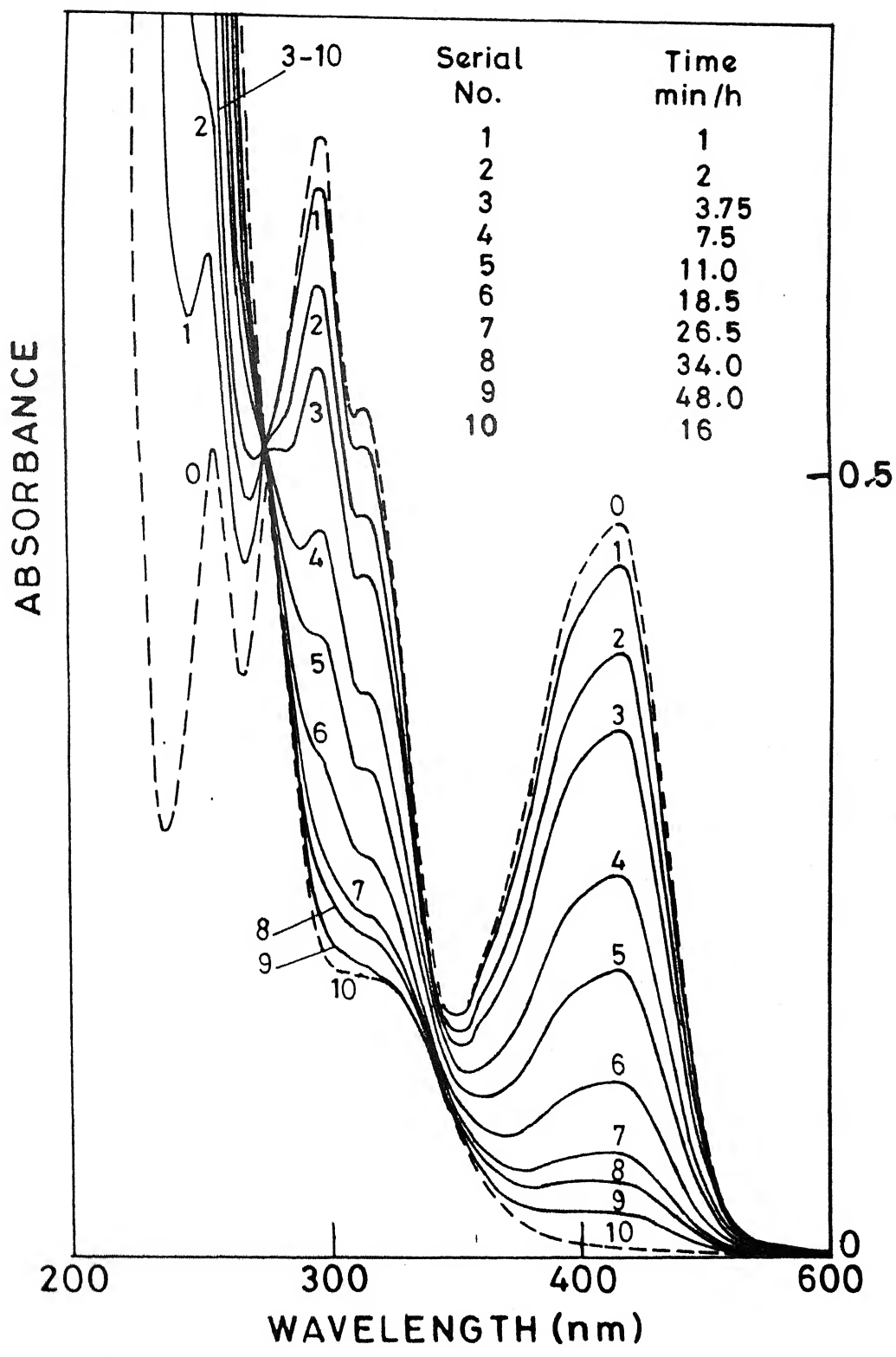


Fig.V.10 Repetitive scans of the reaction mixture during a kinetic run: $[\text{Fe}(\text{CN})_6^{3-}] = 5 \times 10^{-4} \text{ M}$, $[\text{Trien}] = 10^{-2} \text{ M}$, $\text{pH} = 10.5$, $I = 0.1 \text{ M} (\text{KNO}_3)$ and $\text{temp.} = 27 \pm 0.1^\circ \text{C}$.

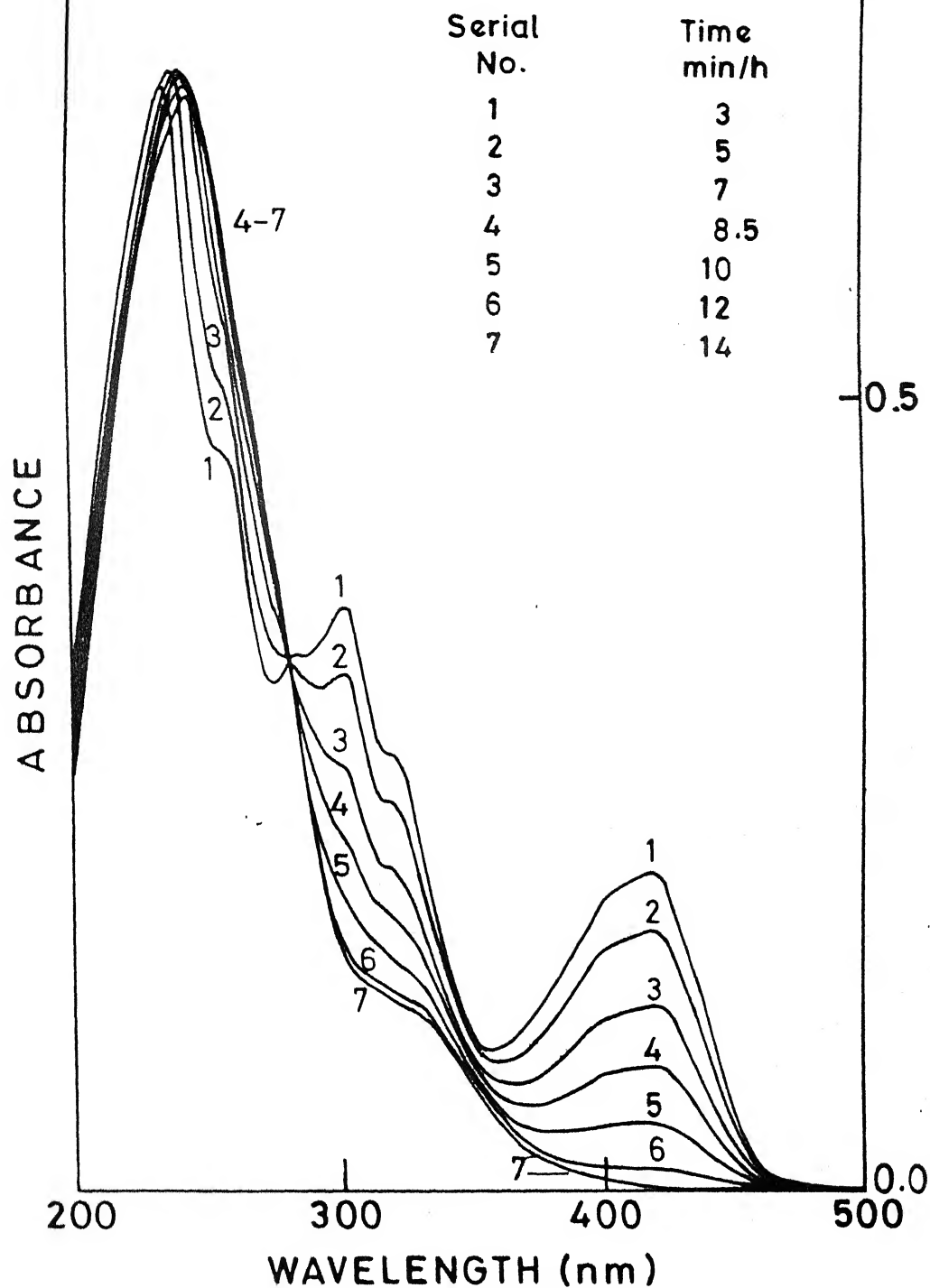


Fig.V.11 Repetitive scans of the reaction mixture during a kinetic run; $[\text{Fe}(\text{CN})_6^{3-}] = 5 \times 10^{-4} \text{ M}$, $[\text{Tet}] = 10^{-2} \text{ M}$, $\text{pH} = 10.5$, $I = 0.1 \text{ M (KNO}_3\text{)}$, $\text{temp.} = 31.5 \pm 0.1^\circ \text{C}$.

Finally, the results on oxidations of polyalkylenepolyamines presented here point to an outer-sphere electron transfer from hexacyanoferrate(III) to polyalkylenepolyamines (P) in a bimolecular step. In the chosen conditions, the reactants are $[\text{Fe}(\text{CN})_6]^{3-}$ on the one hand and P, HP^+ and H_2P^{2+} on the other depending upon the pH of the medium. The respective rate constants have been resolved (Table V.4). The highly negative values of entropy (ΔS^\ddagger) in all the three cases (Table V.5) show that the activated complex, obtained in the bimolecular step is, probably, highly charged. The low values of ΔH^\ddagger is also noticeable because no bond breaking appears to take place during the course of these reactions.

It may be interesting to recall the results of some oxidation studies on amines reported earlier. Pd^{II} , $\text{Au}^{\text{II}4}$ and diphenylselenic anhydride¹¹ oxidise primary amines to corresponding ketones depending on the reaction conditions. Oxidation of $[(\text{R}.\text{CH}_2.\text{CH}_2)_2\text{NH}]$, $\text{R}=\text{Et}$ or Pr by peroxydisulphate under different reaction conditions produce amides, oximes, nitriles, aldehydes and simpler amines as oxidation products.⁵ N-oxide,^{9,10} imines,²⁶ and amides²⁷ and polymeric species¹² have been reported to be the oxidation products of the corresponding amines. The oxidation products of aminocarboxylates viz. EDTA and EGTA have been found to be CO_2 , NH_3 , glycollic acid and the lower amines.¹⁹

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SUMMARY

The first chapter gives a brief literature survey of ligand substitution reactions on Fe(III), Mn(III) and Pd(II) centres. Substitution reactions involving other metal ions viz. Au(I), Pt(II) and Tc(III) have been cited for comparison wherever needed.

The second chapter deals with the substitution reactions between Fe(III) complexes of aminocarboxylates (HPDTA and HIDA) and the cyanide ions. Kinetic data are analysed. The reaction is found to occur in three stages. First is the formation of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ from $[\text{FeL}(\text{OH})^{2-n}]$ complexes, second is the conversion of $[\text{Fe}(\text{CN})_5\text{OH}]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ and third is the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ by the respective ligands released in the first stage. A five step mechanism is proposed for the first stage of the reaction. Besides this, a linear free energy relationship between stepwise rate constants and the respective overall stability constants of the intermediates reacting in these steps has been established.

The third chapter gives a comprehensive report on the substitution reactions of aminocarboxylates (CYDTA, HEDTA and EDTA) complexed to Mn(III) centre by the cyanide ions. A reinvestigation of the MnCYDTA-CN^- system studied by some other workers is

carried out. A six step mechanism is proposed for all the three cases for the formation of hexacyanomanganate(III) from aminocarboxylatomanganate(III) complexes. The penultimate step is rate determining.

The fourth chapter reveals the result of the investigation of reactions of aminocarboxylatopalladate(II) with cyanide ions where aminocarboxylates are EDTA and IDA. A four step mechanism is proposed for the formation of tetracyanopalladate(II) from monoaminocarboxylatopalladate(II) complexes tentatively.

The fifth chapter is a side line of the work embodied in the second chapter. It deals with the oxidation kinetics of reactions of polyalkylenepolyamines with hexacyanoferrate(III). The kinetic data are analysed.

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SUGGESTIONS FOR FURTHER WORK

Ligand substitution reactions are important in many ways. The present investigation underlines the mechanistic pathways of this class of reaction. The mechanism are characterised by a multistep substitution in four, five and six steps for Ni(II), Fe(III) and Mn(III) complexes respectively. Few suggestions for further investigations are given below:

1. Study of kinetics and mechanism of substitution reaction(s)
 - (i) -between $\text{Fe}_2^{\text{III}}\text{L}$ and $\text{Fe}^{\text{III}}\text{L}_2$ (L = aminocarboxylates) and cyanide ions.
 - (ii) -of aminocarboxylatoruthenate(III) complexes with cyanide ion and comparison of the data with that of corresponding Fe(III) complexes.
 - (iii) -on aminocarboxylates complexed to Mn(III) by cyanide ions for confirmation of the Mn(III) chemistry in solution.
 - (iv) -on aminocarboxylates complexed to Pd(II) and Pt(II) by cyanide ions and comparison of the data for the triads.
 - (v) -between ML' (M = Fe(III), Mn(III), Pd(II) and Pt(II) and L' = polyalkylenepolyamines) and cyanide ions.
 - (vi) -of formation of octacyanomolybdate(VI) and octacyano-tungstate(VI) from their complexes of aminopolycarboxylates.

2. Study of kinetics and mechanism of all these above class of reactions in micellar media and comparison of the data with that of in aqueous media.
3. Use of the data (obtained from ligand substitution reactions) to propose a theoretical model for the same.
4. Study of some faster reactions by T-jump and P-jump techniques.

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